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COMPARATIVE MORPHOLOGY AND GENETIC RELATIONSHIPS OF CERTAIN AUSTRALIAN, NORTH AMERICAN, AND EUROPEAN SOILS

C. G. STEPHENS

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1. *Introduction*

MODERN soil science had its origin in Russia in the work of Dokuchaiev and his associates during the last quarter of the nineteenth century. Their recognition of the very great but not exclusive importance of the climatic factor in soil genesis and consequent morphological expression has been the key to the identification of a pattern of broad categories of soils replicated with some variation in areas of similar climates in all continents. The categories are termed Great Soil Groups. The influence of the Russian work was not felt in other countries until the appearance of abstracts in the journal *Geologisches Zentralblatt* in 1901 and the publication in German in 1914 of Glinka's book *Die Typen der Bodenbildung, ihre Klassifikation und geographische Verbreitung*. It naturally follows that the terminology in this field, particularly as it concerns the Great Soil Groups, is dominated by Russian terms such as podzol, chernozem, krasnozem, sierozem, and solonets, with additions such as terra rossa for the reddish soils developed on limestone found commonly in the Mediterranean coastal regions and *Braunerde* for the widespread brown soils of western Europe.

The recognition by the Russians of the non-exclusive role of climate led them to an understanding of local soil differences as a pattern of soil types which can be related to other genetic features such as parent material, vegetation, fauna, topography, drainage, and age of the land surface. These findings relating soils to climate and the other factors of genesis have been stated as three laws of soil distribution. Recently Gerassimov (1945) in discussing the world soil map by Prassolov (1939) gave them the following titles: (*a*) the law of horizontal (latitudinal)

zonality, (*b*) the law of provinciality or regionality, and (*c*) the law of vertical zonality.

In North America soil surveying of a detailed character based on morphological and geological features had been proceeding from before 1900 until it was influenced by the Russian work. Marbut, appreciating the value of the new system, re-orientated the United States Soil Survey and produced both Great-Soil-Group and detailed soil maps of the country (1935). These have been followed by a combined Great-Soil-Group and Soil-Association map by Kellogg (1938). The maps reveal that there is not only a zonation of soils which can be correlated with climatic features, but that there are in addition Great Soil Groups such as prairie, brown, and reddish-brown soils for which there is no precise counterpart in the original Russian classification.

In Australia, Prescott (1931, 1944) by reinterpretation of Australian exploration records and Lands Department data, by using a reconnaissance technique, and by extrapolating from limited areas of detailed soil surveys, has mapped the soils on a scale of 1 in 10,000,000. He named the podzols and solonets soils after the Russian soils of similar character, but largely developed his own terminology for those groups of soils whose precise relationships were not known. For certain of these soil groups he has demonstrated a very close correlation of their geographical distribution with climatic features, most recently with the rainfall-evaporation index $P/E^{0\cdot7}$. In addition, he early recognized that certain ferruginous gravelly soils contained laterite and that these soils, associated with the remnants of a Tertiary landscape, are of a fossil character. These and other soil groups such as terra rossa and rendzina soils, in which non-climatic genetic factors play a dominant or co-dominant part, complicate the Australian soil pattern.

The next stage in mapping the soils of Australia is to identify completely the soils already mapped both in the reconnaissance and detailed surveys, and to attempt a compilation on a scale of the order of one in a million. Since only about 1 per cent. of the continent has been covered by detailed surveys there is, as yet, no opportunity to map soil groups by aggregation of types or other minor categories, and the necessary data for such a procedure will in all probability take something like a century to compile. It thus remains to traverse the country widely but systematically, making direct identifications of higher categories of soils such as Great Soil Groups or the next lower categories, work out relationships of these soils to climate, parent material, topography, drainage, and vegetation, and map on the basis of observation supplemented by interpolations founded on the above relationships. A necessary prerequisite is the identification of the soils already mapped in Australia with their overseas counterparts. For that reason this study comparing the morphology and genetic relationships of Australian soils with those of North America and Europe was undertaken. The observations on which this paper is based were made during visits to the United States of America, Canada, Great Britain and Ireland, and France during the period February to September 1948. In addition use has been made of a collection of soil profiles brought back from Russia to Australia in 1935 by Prescott.

Repeated reference will be made to Prescott's Soil Map of Australia (1944), Teakle's Map of the Soil Regions of Western Australia (1938), and Stephens's Soil Map of Tasmania (1941).

2. *Comparative Morphology and Profile Genesis*

A. *Moor soils*

The general distribution of moor soils in Tasmania, Victoria, and New South Wales is given in Prescott's Soil Map of Australia. A more detailed mapping of their occurrence in Tasmania has been presented by Stephens. They occupy the most elevated parts of the mountain masses of south-eastern Australia, where, together with large areas of bare rock exposure, thin fragmentary skeletal soils, fields of boulders, and mountain-side scree, they make up a typical high-moor landscape.

The soils consist of acid peats, fine and fibrous in the surface horizon and passing to a structureless condition in the sub-soil. They are very variable in depth and overlie fragmentary and partly weathered rock. Occasionally a little mineral soil may be found in the lowest horizon. These soils are normally wet and poorly drained for the greater part of the year, not necessarily because of poor topographical drainage but rather because of the sponge-like character and high water-holding capacity of the peat. They are associated with an alpine flora of mosses and low shrubs.

Very similar though generally deeper peat soils occur on the heather-clad moors of Great Britain and Ireland, reaching their maximum development on the highlands in Scotland. They have recently been described in detail by Fraser (1948). Profile morphology, topographical association, and drainage characteristics appear to be the same. Above a certain elevation the nature of the underlying rock appears to be of no great significance in their formation, but their occurrence at lower elevations appears to depend to some degree on the presence of material of low base status. An example of the latter is the extensive area south of Lough Neagh in Northern Ireland.

A similar though shallower peat soil occurs on the top of Clingman's Dome in the Great Smoky Mountains on the border between Tennessee and North Carolina in the U.S.A. It is associated with an alpine-forest and moss flora. The United States Soil Survey has named no category of high-moor peat soils.

On the moors of both Scotland and Ireland occur profiles in which the peat is shallower than usual, though frequently over a foot deep, and in which it overlies an obvious former podzol profile. The upper portion of the B horizon contains a thin but continuous pan above which weak gley-like characteristics are present in what was formerly the A_2 horizon. Although occurring on quite steep slopes the surface horizons of these soils appear to be saturated with water, a condition favourable for the accumulation of the peat.

These profiles provide an explanation of the genesis and morphology of a group of organic soils occurring widely in western Tasmania and to a much lesser degree in favourable situations in Victoria. In Tasmania, where they are termed button-grass plain soils, from their pre-

dominantly Cyperaceous plant association, their distribution has been shown by Stephens. They occur in humid localities on a variety of parent materials largely of low base status, and range from the elevated moors mentioned above nearly to sea-level. The mineral profile beneath the peat consists of a podzol, the prominent features being a hardpan either of iron and organic matter in the B_1, or an indurated A_2 horizon. These cause waterlogging and the ultimate accumulation of a peat surface frequently up to one foot thick, usually partly fibrous and partly decomposed. They are extremely acid in reaction, pH values as low as 3·5 being frequently recorded.

From the above observations there would appear to be two significant categories of soils whose morphology is strongly influenced by the accumulation of plant remains largely under conditions of primary normal drainage. They could appropriately be referred to as high-moor peat and moor-podzol peat.

It is apparent that if organic matter accumulates in unusually large amounts in a soil its rate of oxidation and decomposition must be low. It is equally obvious that the genesis of the two kinds of soils is not precisely the same. The high-moor peat accumulates essentially because of a low rate of decomposition which is a result of low mean annual temperature and consequently is usually found at high altitudes. This is well illustrated by the occurrence of such soils on the central plateau of Tasmania, where, on the eastern side, it extends into a region characterized by climatic features such as precipitation and saturation deficit typical of the podzol zone. Temperature is low, however, and organic matter, despite its slow rate of production, accumulates because of an even slower rate of decomposition. Obviously the genesis of such soils will be hastened by restricted primary drainage, and probably the deepest of the high-moor peats have this factor operating in their genesis.

The moor-podzol peats appear to be polygenetic. First a podzol develops: this is followed at maximal development by hardpan formation causing frequent and prolonged saturation of the upper horizons of the soil profile: this induces anaerobic conditions similar to those prevailing in swamps, and consequently organic matter accumulates.

On the moors themselves it is apparent that, depending on the drainage status of the site or the soil, either one or both of the above processes may be involved. The high-moor peat is a low-temperature peat sometimes modified by restricted primary drainage. The moor-podzol peat is a restricted secondary-drainage peat whose genesis is augmented at high elevations by low temperatures and at low elevations by parent material of low base status.

B. *Podzols and podzolic soils*

Since the early adoption by soil scientists of the word 'podzol' to describe leached and acid soils with ashy-grey surfaces and pronounced profile development, a marked extension of the usage of the adjectival form podzolic has taken place. This has facilitated the naming and classification of soils which, though not conforming strictly to the

morphology of the original podzol, possess a number of profile characteristics and genetic features which readily identify the soils as being closely related in both morphology and development to the podzols proper. Certain of the soil names used, for example red podzolic, appear to be a contradiction in terms, but the use of the adjectival form to denote recognizable relationships together with another word to describe a pronounced characteristic of the soil and, further, the adoption of a definite connotation overcome such difficulties. This type of terminology has been exclusively adopted in North America and partly in Europe. Such soils have been widely recognized in both continents and extensively mapped in detail in the former.

In North America the following are recognized: podzols, grey-brown podzolic soils, brown podzolic soils, red podzolic soils, and yellow podzolic soils. In Europe there is a general recognition of podzols and brown podzolic soils and a supplementary use of such terms as 'weakly leached' or 'podzolized' soils. In Australia a wide range of soils was first covered by the term podzol but in recent detailed soil-survey work there has been recognition that some of these soils belong to the podzolic categories.

A comparison of the podzols and podzolic soils in the three continents shows a marked identity in the recognized characters of the A_2 and lower horizons in the profile. In the podzols the A_2 is invariably light grey in colour; the B_1 horizon may consist of *orterde* and/or *orstein* (and/or *alios* in France, where it sometimes assumes massive proportions reminiscent of Buchanan's laterite); the B_2, if present, of an accumulation of clay with which there may be an iron pan, all clearly distinguished in colour and texture from the above horizons; and the C horizon of very variable character depending on the nature of the parent material. In the podzolic soils the A_2 horizon although characteristically light in colour may be brownish-grey or yellowish-grey; the B horizon is purely a zone of clay accumulation; and the C horizon is variable in character according to the nature of the parent material. Apart from the colour of the A horizon the colour and structure of the B horizon are the principal determinants of the group to which the soils belong, the grey-brown podzolic soils being characterized by brown B horizons, the brown podzolic soils by brown to yellowish-brown B horizons, the red podzolic soils by red, and the yellow podzolic soils by yellow B horizons.

In marked contrast to the identity of the lower horizons the A_1, and the organic A_0 and A_{00} horizons exhibit marked differences between the three continents, particularly between Australia and the other two. In North America and Europe under natural conditions the A_{00} or litter horizon is always well represented, frequently being some inches deep. It is largely composed of leaves or pine needles, and it is somewhat variable in depth and degree of decomposition depending on its composition and the season of the year, the autumn and winter being seasons largely of accumulation and the spring and summer periods of decomposition and destruction. In Australia, where the forest and shrub vegetation is almost entirely of a sclerophyll character with litter fall slow and relatively continuous, and where the podzolic soils extend into

areas where grass species are widely present, the A_{00} has a different character. For much the greater part it is thin and discontinuous and frequently composed as much of twigs and bark as of leaves. In the very restricted extremely humid areas of western Tasmania and coastal Queensland where genera such as *Nothofagus* occur and create a rain forest the litter assumes a more leafy, continuous, and deeper character.

In North America and Europe the horizon of organic decomposition —the A_0—is invariably present: it may be as little as $\frac{1}{2}$ in. thick. In Australia it has not been recorded under natural conditions. It is certainly absent in all but the rain-forest areas: it may occur there, but no published descriptions of podzols and podzolic soils indicate its presence.

In North America the upper mineral and organic horizon—the A_1—is generally thin, usually about 1 in. thick, and this feature is there regarded as characteristic of podzols and podzolic soils. In western Europe there is a rather wide variation in the thickness of the A_1 horizon (from 1 to 8 in.), but it is generally thin. In Australia the A_1 is generally thick, frequently more than 6 in.; but there are widespread occurrences of soils with thin A_1 horizons, particularly on soils derived from remnants of laterite formations and on others which appear to have suffered a cycle of recent natural erosion.

It would, indeed, be surprising if the organic horizons of Australian podzol and podzolic soils were identical with those of the northern hemisphere, considering that Australian forest and shrub vegetation is almost entirely sclerophyll and evergreen in character compared with the mixed deciduous mesophyll, sclerophyll, and needle character of that in the northern hemisphere, and considering also the vastly different insect population of Australian soils in which ants and termites rather than earthworms play a predominant role, and the fact that fire has always undoubtedly been a natural feature of Australian forests and grasslands, so much so that most species, particularly the Eucalypts, are fire-resistant. That the soils are truly podzolized and therefore genetically and morphologically closely related to those of the northern hemisphere is indicated clearly by the chemical and physical characteristics of the mineral profile and by the development of northern-hemisphere type A_{00} and A_0 horizons when various exotic species are planted. For example the Mt. Burr sand of south-eastern South Australia, with thin A_{00}, no A_0, and thick A_1 horizons under the natural dry sclerophyll forest dominated by *Eucalyptus obliqua* and *E. Baxteri*, when planted to *Pinus radiata*, rapidly develops characteristic northern-hemisphere type A_{00} and A_0 horizons.

In brief, Australian podzols and podzolic soils exhibit deviation from those of North America and western Europe in their phytologic and phytophagic characteristics, this deviation being largely due to difference in biological associations and relationship.

C. *Black soils: Chernozems, Black Earths, Prairie Soils, and Wiesenböden*

Prescott's map of Australia shows black soils (rendzinas and black earths) stretching from tropical Queensland to Tasmania and the lower south-east of South Australia. The latter area, as shown by Stephens

(1941) and Crocker (1944), is occupied by rendzinas which are discussed in another section. There are other small areas of black soils in the red-brown earth zone in South Australia, for example at Saddleworth, and restricted occurrences in Victoria, near Melbourne and at Coleraine. There is a notable absence of black soils in Western Australia. Although Teakle (1936) established a theoretical zone of red-brown earth in that State, and Prescott (1949) has shown the need to consider together black earths and red-brown earths in the establishment of his Australian soil-zone index $P/E^{0.7}$, there is in fact no significant geographical expression of either of these soil groups in Western Australia largely because of the widespread occurrence of fossil soils associated with laterite and later derivatives of these. In both North America and Europe the corresponding chernozem and chestnut soils zones lie in juxtaposition, but are geographically distinct.

As in eastern Australia, the black soils of North America occur over a wide range of latitude extending from central Alberta to southern Texas. There they are termed chernozem, prairie, and reddish prairie soils. In Europe the distribution of the classic *chernozem* covers a much more restricted latitudinal range and there appears to be rather less variation in the individual soil characteristics, although the Russian pedologists have long recognized such sub-categories as degraded, thick, thin, fat, and southern chernozem. However, it appears, if the degraded chernozem is excluded, to have consistently an organic-matter content of 4 per cent. or more in the surface soil and to have a stable fine-crumb to small-nutty structure.

These features are present in the northern areas in North America, but an obvious coarsening of structure and lower organic-matter status is a feature of these soils in Texas. In Australia it is doubtful if such features are to be found consistently outside Tasmania. In the largest area of black soils extending from New South Wales to central and northern Queensland, structure varies from fine crumb to coarse blocky, and organic matter in the surface soil is usually below 4 per cent. However, the textural and calcium-carbonate profile of these soils is identical with the chernozem and the close relationship is obvious. Moreover, there appears to be no geographical inflection in the organic-matter status and structural characteristics of these soils that would readily enable their separation into two groups. Nevertheless, some such separation appears to be required in Australia and North America, and the less organic category, if established, would also probably accommodate the sub-tropical black clay soils of South Africa reported by van der Merwe (1940) and the Indian soils termed 'regur' which have been compared with Australian black earths by Hosking (1935). A problem in nomenclature is thus automatically created, and it is suggested that it be met by regarding chernozem as the soils of the more organic category and black earths as those of the less. These, together with the prairie soils referred to below and the rendzinas, could all simply be termed black soils.

In North America widespread soils termed prairie and reddish-prairie have been extensively mapped in the zone between the podzolic soils

and chernozems. From their extent they would appear to be truly regional soils, but an examination of profile morphology reveals weak but consistent and significant hydromorphism in the form of subsoil mottling. This is a result of a gently rolling topography in a climate which at certain periods is wet enough to cause temporary waterlogging. These conditions are reflected in the grassland association of these soils and, where the steeper sites provide adequate drainage, by the appearance of grey-brown and other podzolic soils clothed by trees. The prairie soils are non-calcareous in the soil profile, but where formed on deep parent material, such as loess, lime nodules may be found at some depth. In general morphology they resemble profiles of degraded chernozems in the 'Moscow Collection' brought back from Russia by Prescott to Australia in 1935. They are simply weakly hydromorphic black soils clearly related to *Wiesenböden* which have a more scattered distribution. This is a reflection of their association with areas of very restricted drainage; so much so that lime is generally retained in the profile and mottling of the subsoil is much more pronounced and drabber in colour than in prairie soils. So far prairie soils have not been recognized in Australia.

D. *Red-brown earths and chestnut soils*

Lying in the sub-humid areas of eastern Australia is a group of soils which Prescott (1931) termed red-brown earths. These soils have a characteristic morphology: A horizons reddish-brown in colour and of various textures; B_1 horizons generally of prismatic structured red clay; B_2 horizons of calcium carbonate, partly soft and partly nodular, in a clay matrix; and C horizons of various types derived from a wide range of parent materials. In mapping the soils of Tasmania, Stephens, because of a lack of reddish colour in the surface soils, termed the counterpart of these soils in that State brown earths.

Comparison of these soils with the reddish-chestnut and chestnut soils of North America indicates that they are morphologically similar. In particular the red-brown earths correspond well in colour, structure, and textural contrast of horizons with the reddish-chestnut soils. This is well exemplified by the features of a profile of Webb loam, a reddish-chestnut soil examined some miles south of San Antonio in Texas, U.S.A., which has almost identical morphology to the Urrbrae loam,* the red-brown earth of the experimental fields of the Waite Agricultural Research Institute in Adelaide, South Australia, the type locality (on the score of climate as well as morphology) for this group of soils. There is little doubt that the similar limited comparison possible between the brown earths of Tasmania and the chestnut soils of North America is valid, although the restricted area of such soils in Australia does not facilitate a good comparative study.

From a comparison with two profiles of chestnut soils (kashtanozem) from the Volga region in Russia and from the observations of Prescott

* The Urrbrae loam, when seen by C. E. Kellogg, Chief of the United States Soil Survey, in January 1949, was also identified by him as corresponding to a reddish-chestnut soil.

(1949) and Nikiforoff (1948), there appears to be some considerable difference between these Russian soils and their presumed Australian and North American counterparts. The Russian soils have A horizons which are heavy textured and are dark brownish-grey in colour, the resemblance to a chestnut in colour being quite remote. The B horizons are pale brown in colour and highly calcareous. On the Munsell colour system these Russian chestnut soils have A horizons approximately 10 YR/4/2 in hue, value, and chroma respectively, whereas the red-brown earth A horizons from soils in South Australia approximate 2·5 YR/5/4. Corresponding values for B horizons are 10 YR/7/3 and 2·5 YR/4/6.

In both North America and Europe the chestnut and reddish chestnut soils lie in zones separate from the chernozems. In each case the chestnut zone is slightly drier than the chernozem. In Australia both the black earths and red-brown earths and the black soils and brown earths of Tasmania occupy the same geographical and climatic zones and, as mentioned earlier, Prescott has found it necessary to consider them together in the development of his climatic soil index. The soils occur together in Queensland and northern New South Wales, the black earths dominating the pattern. In southern New South Wales, Victoria, and South Australia the red-brown earths predominate. In Tasmania the black soils and brown earths appear in some districts together and in others apart. Where together they are in roughly equal proportions. Texture, probably as a characteristic inherited from parent material, and, to a lesser degree, topographical position appear to be the determining factors in the soil developed on any site, heavy texture and low position favouring black earth formation and medium to light textures and elevated sites favouring red-brown and brown earth formation.

E. *The desert soils and the soils of semi-arid regions*

The soil map of Australia reveals a marked zonality; there is a strong climatic correlation in the soils of both the humid to sub-humid region and of the extensive central arid area. However, the soils of the semi-arid area lying between the red-brown earths and black earths on the one side and the desert loams and related soils on the other show but little evidence of similar zonation, and, in fact, present a pedological problem with morphological, genetic, and geographical facets. The soils are: brown soils of light texture, grey and brown soils of heavy texture, solonized brown soils, mallee sandhills, and solonets soils. The occurrence of the solonized brown soils and associated mallee sandhills with their localized, though widespread, calcareous parent material has been elucidated by Crocker (1946), and the solonets soils are to be expected in a zone of imperfect leaching and high incidence of cyclic salt. The brown soils of light texture and the grey and brown soils of heavy texture epitomize the problem.

A key to the solution of this problem is provided by the only area where the red-brown earths lie in juxtaposition to the desert loams—namely between Port Augusta and Peterborough in South Australia. Here in the vicinity of the 14-in. rainfall isohyet a theoretically ideal

change in profile characteristics is presented in nature. Over a distance of a few miles there is a change in colour and textural and structural morphology, the typical red-brown earth giving way to desert loam soils with dull, reddish-brown surface soils of shallow depth and heavy texture overlying a B_1 horizon of coarsely structured red-brown clay, a B_2 horizon with little lime, and a B_3 horizon containing gypsum.

In all other areas the counterpart of this region of morphological change is enveloped by a wide zone of the brown soils of light texture and grey and brown soils of heavy texture which in New South Wales and Queensland, the principal areas affected, extends from about the 16-in. to the 10-in. isohyet, and in the case of the latter soils frequently follows the wide braided courses of the seasonal streams far into the desert areas.

Throughout the areas of their occurrence these heavy soils are, where grey, still subject to intermittent inundation and, where brown, either liable to infrequent inundation or have been very recently released from such inundation because of generally very slightly higher relief. Both the brown and grey soils are of weak textural profile development and contain lime and gypsum in the profile. The brown soil appears to have but recently thrown off the cloak of hydromorphism and the grey soil is still definitely hydromorphic. The parent materials of these soils persist into the black earth and red-brown earth zone, and the lower, poorer drained sites are occupied by grey soils of heavy texture, as has been shown in surveys by Smith (1945) and Butler (1942) of the red-brown earth zone of the Riverina of New South Wales. Similarly, the grey soils of the Wimmera district of Victoria represent this group and are the hydromorphic equivalent of the associated red-brown earths of the better drained sites. Just as *Wiesenböden* represent the hydromorphic counterpart of prairie and chernozem soils, so grey soils of heavy texture appear to be the hydromorphic counterpart of red-brown earths, black earths and, perhaps, desert loams. It is significant that the more elevated sites in the widespread area of the grey and brown soils of heavy texture, in the Wakool irrigation area of New South Wales where the rainfall is in the vicinity of 14 to 16 in., are occupied by red-brown earths.

In contrast to the grey and brown soils of heavy texture the brown soils of light texture occupy areas which are slightly elevated and rolling, are typified by a generally weakly developed stream pattern, and appear to be low remnants of a former land surface. The soils, which are brown to red-brown in colour on the surface, brighten to red and become heavier with depth. They are generally slightly acid in reaction, contain little or no lime and no gypsum. Morphologically they convey the impression, strengthened by their topographical character, that they are soils of somewhat relict nature belonging to a former wetter era, probably being modified red-brown earths or red podzolic soils, most likely the latter. There is a distinct possibility that the two major regions in New South Wales occupied by these soils represent slightly elevated areas to be correlated with the last of the Pleistocene glaciations in south-east Australia which, though not affecting by actual ice-cap conditions any adjacent mountains, would have yet exerted a pluvial and geo-

morphological influence as far north and west as the area occupied by these soils. Where they occur in tropical Australia their topographical relationships are not fully known. The morphological resemblance of these soils to some of the non-calcic brown soils of the western United States that occupy terraces and other relict landscape features to a significant extent suggests a parallel morphological and evolutionary history worthy of detailed study.

Just as the residual or lateritic podzols are the fossil soils of the humid zone and the desert sandplains the fossil soils of the arid zone, so the

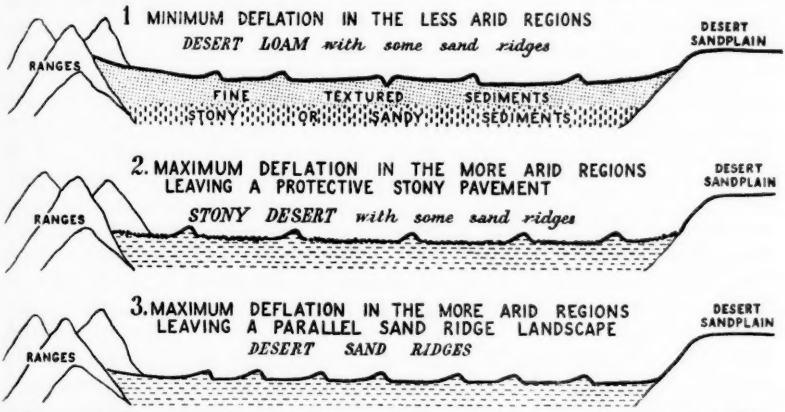
1 MINIMUM DEFLATION IN THE LESS ARID REGIONS
DESERT LOAM with some sand ridges
DESERT SANDPLAIN
RANGES
FINE TEXTURED SEDIMENTS
STONY OR SANDY SEDIMENTS
2. MAXIMUM DEFLATION IN THE MORE ARID REGIONS LEAVING A PROTECTIVE STONY PAVEMENT
STONY DESERT with some sand ridges
DESERT SANDPLAIN
RANGES
3. MAXIMUM DEFLATION IN THE MORE ARID REGIONS LEAVING A PARALLEL SAND RIDGE LANDSCAPE
DESERT SAND RIDGES
DESERT SANDPLAIN
RANGES

FIG. 1. Idealized cross-section diagrams showing the general structure of the landscape in the arid regions of Australia and the relationship of the different soils of the landscape to topography, nature of deposited material, and deflationary power of the climate.

brown soils of light texture appear to be the fossil soils of the sub-humid to semi-arid zone.

The fully arid areas in Australia are occupied by desert loams, stony desert, desert sandhills, desert sandplain, and significantly large areas of rough tableland and ranges. The desert sandplains are definitely large remnants of former soils and landscapes from a more humid period. They are composed of soils showing silicified and lateritized features which provide by erosion a large proportion of the material for the lower floor of the desert proper. Not only do these desert sandplains occur in the large areas indicated on Prescott's map, but smaller remnants consisting of mere vestigal flat-topped and pointed hills are common throughout the arid region. The relationships of these plateau remnants, the stony ranges, and the desert soils proper, namely desert loams, stony desert, and desert sandhills, to the fluvial genesis of the desert floor, to the degree of deflation correlated with the degree of aridity, to the stabilizing effect of stony pavements and to the more or less mobile sand-ridges are shown in Fig. 1. There is an obvious resemblance to the genesis of the soils and other features of the Sahara as detailed by Gautier (1935). The above groups of soils represent three

degrees of balance between the eroding and depositional process. Accordingly the desert loams are found on the slightly less arid periphery of the desert where rainfall ranges from about 11 in. to 6 in.; and the stony deserts and desert sandhills in the central extremely arid areas where rainfall is less than 6 in. and wind erosion so intense that elutriation of finer particles is generally complete. In the case of the stony deserts the surface pebbles, which are in large part composed of siliceous material derived from the relict areas, show a dark coloured and intense 'desert varnish'.

In textural and structural morphology these soils do not appear to differ radically from their European and North American counterparts, the nature and distribution of the various horizons, including those of lime and gypsum, appearing to be comparable. However, there is a marked dissimilarity in colour. There is, of course, no possible comparison with the grey desert soils of the arid areas of the north-western States of U.S.A. nor with the sierozem of Russia, the absence of such soils in Australia doubtless being due to a lack of cold, dry desert conditions, the lowest recorded annual rainfall in areas of moderate temperatures being 18 in. at Ross in Tasmania, where brown earths largely occupy the landscape. Nor is there a good colour comparison with the so-called red desert soils of the south-western States of U.S.A. nor with the brown soils of the arid steppes of Russia. In Australia the desert loam soils vary in surface colour from reddish-brown to bright red with progressive aridity; the soil material beneath the stony surface of the stony desert is also red and the sand-ridges of the desert sandhills are a brilliant red. Colours mainly lie on the 2·5 YR and 10 R charts of the Munsell colour system. The red desert soils of U.S.A. vary from pale brown to weak red-brown in colour, the whole impression being one of pastel shades (5 YR and 7·5 YR), in contrast to the brilliant hues of Australia. Similarly an alkaline brown soil (10 YR) from near Lake Elton on the Kirghiz steppes in Russia offers no colour comparison. The red desert soils of U.S.A. lie in an area with a climate very comparable with that of the Australian deserts. The differences in the soils are probably to be correlated with different topographical conditions. As shown in Fig. 1 the Australian desert is composed of a simple floor probably largely of post-Pleistocene age set between stony ranges and remnants of a Pliocene landscape. The American desert floor appears to be largely composed of a series of terraces correlated with the Pleistocene glaciations and a very juvenile region associated with the stream courses. The paler colours may therefore be a reflection partly of senescent and partly of juvenile soil features.

F. *Red loams*

To an appreciable extent in the more humid parts of all the eastern States of Australia and to a minute extent in similar parts of South and Western Australia there occur deep red to chocolate-coloured, friable, and permeable clay soils. They are variously known as volcanic soils, chocolate soils, and red loams. These names are in some degree misnomers, but scientists in Australia have preferred to use the name red

loams, largely because of their red or dark red-brown (chocolate) colour and the loam-like character of the friable clay. Their distribution in Tasmania has been mapped by Stephens (1937) and in Australia generally by Prescott, but they are much more common in coastal Queensland than shown on the latter's map of Australian soils.

Soils of very similar morphological features occur in U.S.A. In California the Aiken, Olympic, and Sites series and in the southern and eastern States the Nachodoches, Decatur, and Davidson series are examples of these soils which have been mapped extensively. Generally, soil workers in U.S.A. have termed these soils lateritic because of the narrow silica-sesquioxide ratio of the clay fraction and for purposes of classification at higher categories have included them with the yellow and red podzolic soils—this despite the fact that they bear no physical resemblance to Buchanan's laterite and lack the pronounced A-horizon development of the red and yellow podzolic soils in both colour and texture. However, the present trend is to place them in another group and, adopting a compromise in terminology, to call them latosols. This has resulted, in part, from the work of Cline (1947) and Hough (1937, 1941) and their associates on similar soils in Hawaii. There it has been shown that, under the conditions of weathering necessary to produce these soils, titanium and iron oxide are retained in the soil and, depending on the intensity of the weathering process, aluminium may be present either as kaolin or as hydrated alumina. These soils are characterized by low and very low silica-sesquioxide ratios. Similar data for islands in the southern Pacific have been presented by Grange (1949), and recent unpublished data on similar soils from Queensland suggest by the low cation-exchange status that these soils have related properties.

One outstanding feature of these red loams or latosols is their occurrence over a wide climatic range, for example from Virginia to Hawaii in U.S.A. and from temperate Tasmania to tropical coastal Queensland in Australia. The following thesis regarding their genesis takes account of this distribution in eastern Australia.

In temperate areas they are restricted in occurrence to the most basic rocks such as basalt and its close relatives: for example, solely on basalt on the north-west coast of Tasmania. In tropical areas they occupy a much greater proportion of the landscape and occur on a wide variety of parent materials, in fact, on all but the most siliceous rocks: for example, around Cairns in north Queensland, on basalt, on dark coloured schist, on transported colluvial material of mixed origin, and on some granites.

Red loams are almost invariably deep and clayey soils and, since some of the basalts on which they occur are very young, the rate of chemical weathering of the parent rock must be high. They are in a flocculated state, thus being well protected against erosion and against the development of a podzolic type of profile. The clay in these soils is partly composed of and flocculated by hydrated ferric oxides. Therefore the rate of weathering with its consequent production of ferric oxide must be faster than the podzolization process which would cause translocation

of the sesquioxides in the soil profile and be accompanied by a degree of deflocculation. Two major factors determine this rate of weathering; the ease of weathering of the rock and the climate. If the rate of weathering is sufficiently great hydrated ferric oxide will be produced at a rate sufficient to prevent deflocculation of the soil and so preserve it against podzolization, the resultant soil being a red loam. If the quantity of hydrated ferric oxide produced is too little to maintain flocculation, then podzolization will result, red podzolic soils being produced where the process just favours the podzolic soils.

Searle (1923) states: 'The rate of weathering depends chiefly on the nature of the rock and/or the character of the weathering agencies.' There appears to be no well-recognized classification of rocks in terms of their ease of weathering except that basalt is regarded as one of the most easily weatherable rocks, and that slow weathering is associated with high silica content. The function of protoxides in weathering has been summarized by Merrill (1897), who states '. . . the ordinary processes of decay in siliceous rocks containing ferruginous protoxide and alkalies consists in the *higher oxidation and separation of the protoxides in the form of hydrous sesquioxides* and a general hydration of the alkaline silicates accompanied by the formation of alkaline carbonates which being readily soluble are taken away nearly as fast as formed. More or less silica is also removed. . . .'

Szymkiewicz (1947), using van't Hoff's law, has developed a climatological index (τ) which because of its origin is very appropriate to use as an index of chemical weathering power of the climate. It is stated as $\tau = 2{\cdot}5^{t/10}$, where t is the temperature of the air in degrees centigrade, giving an index of 1 for 0° C.

At Moina in Tasmania, which is chosen as climatically characteristic of the Surrey Hills area where soils formed on the Tertiary basalt show some degree of profile formation of the podzolic type, as observed by Stephens (1941), the mean annual temperature is 9° C. and the index $\tau = 2{\cdot}28$. At Stanley in Tasmania, which is characteristic of the lower areas where red loams occur on the same tertiary basalt only and all other rocks give rise to podzols and podzolic soils, the mean annual temperature is 15° C. and the index 3·95. At Cairns, where only the most siliceous rocks and transported materials give rise to podzolic soils, the remainder being covered by red loams, the mean annual temperature is 25° C. and the value of the index 9·88.

It would appear that the criterion determining the presence of red loams is the sum of the effects of the weathering power of the climate and the ease of weathering of the parent rock, the latter being correlated with the abundance of iron-bearing minerals in relation to the feldspar and silica content. The result is that in areas of low weathering power no red loams are formed, in areas of moderate weathering power red loams are formed only on basalt and rocks of similar iron-mineral content, and in areas of high weathering power red loams are formed on a wide but not comprehensive variety of parent materials.

The genesis and distribution of these soils may be summarized in the following diagram (Fig. 2).

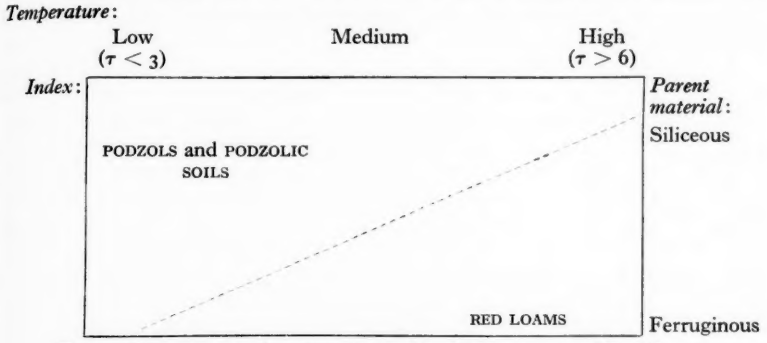

FIG. 2. Diagram showing the relationship of occurrence of Red Loams to temperature, weathering index, and rock character.

G. *Rendzinas and related soils: fen peats*

Rendzinas, which are frequently referred to as 'lime-humus' soils, were originally identified and named in Poland and western Russia. Since then they have been recognized over wide areas in western Europe and to a more limited degree in North America, Africa, and Australia. Their very characteristic morphology of a shallow, black, medium to heavy textured soil resting on calcareous parent material makes the identification of modal representatives of this group a simple matter. In Australia they occur most commonly in two areas in South Australia. In the lower south-eastern part of that State they occur extensively on generally low areas of Miocene polyzoal limestone. In restricted areas this material is above the influence of the ground water and the rendzina soils appear to be normal, and compare well in all morphological features with those seen in various southern areas in England and in the district of Maine and Loire and the Mediterranean coast in France. In the greater part of the area the limestone and soil are within the influence of the seasonally fluctuating water-table, and although the profile of this soil—the Millicent clay described in detail by Stephens *et al.* (1941)—has normal textural and structural rendzina morphology it, doubtless, should be referred to as a water-table rendzina.

Where the moisture status is so high that completely hydromorphic or swamp conditions prevail, then fen soils are produced. A comparative study of the soils and vegetation of the Eight Mile Creek Swamp of South Australia was made by Stephens (1943) and Eardley (1943). The soils proved identical with those of the English fens, and vegetation, although of different species, was formed into associations which closely paralleled in facies and function those found on the English fens.

As the Millicent clay extends northward into areas where the climate is somewhat drier and cyclic salt is retained to a greater degree it changes from a definite black to grey and there is some profile development. Farther north the change is definitely to solonets morphology. The intermediate stage could well be referred to as a category of degraded rendzinas or perhaps solonized rendzinas. Through both areas there

are, as is to be expected, occurrences of solonchak and a common development of salt pans.

A second area where rendzinas are common is on the western slopes of the Mount Lofty ranges which are largely composed of folded and faulted pre-Cambrian sediments including some highly calcareous members. The latter, in the vicinity of Adelaide, give rise to characteristic shallow black soils, but towards the northern and increasingly drier areas there is a significant change in morphology. The soil remains shallow, being about a foot in depth, but the surface few inches become grey or pale brownish-grey in colour, the sub-surface remaining black. These soils, of which a representative, the Yangya silty loam, has been described by Stephens *et al.* (1945), are not sufficiently saline to ascribe this apparent degradation to solonization under present climatic conditions. In still drier areas of less than 12 in. annual rainfall the black sub-surface disappears from the profile leaving a shallow, brownish-grey, powdery calcareous soil. Such a soil, from Melton in South Australia, has been described by Prescott and Skewes (1938). It would appear that this is a representative of another calcimorphic soil group of low organic-matter status due to the dryness and insolation of the arid climate. It is suggested that it be termed 'grey-brown calcareous desert soil'. The Yangya silty loam represents a transition from the true rendzina to this soil group, and it is proposed to refer to such soils as 'grey calcareous soils'. In tropical Australia there are rendzinas on Tertiary limestones.

Another variant from the usual concept of a rendzina is that occurring with rendzinas and terra rossa soils on the Mediterranean coast of France, and was seen in company with G. Drouineau of the Agronomy Research Station at Antibes, who simply referred to it as a 'rendziniform soil'. This soil is yellow-grey to yellow in colour and is deeper than usual for rendzina soils. It is possible that the yellow colour is inherited from the parent material and hence may be considered lithochromic. No soil similar to this has been noted among the Australian variants of the rendzina soils.

H. *Terra rossa and related soils*

In the period 1937–40 detailed soil surveys by Stephens and others (1941) and a reconnaissance by Crocker (1944) in the lower south-east of South Australia mapped and described three series of shallow red-brown soils developed on limestone. They were found in association with rendzina and podzolic soils. Because of this association and their apparent similarity in colour and other morphological features they were thought to be related to the terra rossa of Mediterranean countries. Other soils with similar morphology have since been seen in the region of Adelaide where they are located on calcareous members of a series of pre-Cambrian rocks.

In the vicinity of Antibes in southern France, where terra rossa soils are well-developed, there are soils with similar morphological features and geographical associations to those found in South Australia. In colour, structure, and textural characteristics the terra rossas at Antibes

are very similar to the heavy textured members of the Coonawarra series of South Australia. In the Antibes region the chief variation from normal morphological features is a darkening of the surface readily traced to additions of dark-coloured material from rendzina soils farther upslope. In the lower south-east of South Australia the principal variation from normal is due to additions of sand from the adjacent podzolized dune sand, thus accounting for the generally lighter textured Hindmarsh and Warralong series and the light textured members of the Coonawarra series. All these soils have the small ferruginous concretions frequently found in soils of the group.

The Crawford clay seen in southern Texas also has morphological features identical with the Mediterranean terra rossa and is associated with areas of rendzinas.

This association of terra rossa and rendzina has been frequently noted and in all cases so far seen the terra rossa is developed on the harder parent limestone and the rendzina on the softer. However, in some cases, and this is notable in the lower south-east of South Australia where polyzoal Miocene limestone is one of the parent materials, the hardness found in association with terra rossa soils on this rock is due to secondary calcification and takes the form of a hard layer or skin superficially formed on the softer rock and usually only 1 or 2 in. thick.

In the moister regions of Europe away from the Mediterranean Sea, rendzina soils are found in association not with terra rossa but with a group of soils long referred to as *Braunerde* and also known as brown forest soils. These are a simple replacement of terra rossa under a more humid environment and in association with mesophyllic forests. Although generally browner in colour and with more organic matter in the profile, there are occasional examples which bear a strong resemblance and are obviously related to terra rossa as exemplified by a dark red-brown soil shown to the author by Professor G. W. Robinson on Carboniferous Limestone at Penmon in Anglesey, Wales. Brown forest soils have not been reported in Australia, and it is very probable that the absence of mesophyllic species in areas of suitable climate precludes their formation.

A group of soils found very commonly in the semi-arid parts of southern Australia is the mallee soils formerly so named because of a marked association with several species of dwarf eucalypts commonly referred to as mallee. Later Prescott renamed these soils brown solonized soils. They are found almost exclusively in association with limestone which Crocker (1946) postulated to be of aeolian loessial character and is therefore known as aeolianite. These soils bear some resemblance to terra rossa but are duller in colour and lack the structural features so pronounced in terra rossa. Morphologically they correspond very closely to the reddish-brown soils of southern United States that are also found on deep layers of highly calcareous material in semi-arid areas. This calcareous parent material, generally known as 'caliche' in the United States, is regarded as being of hydrological origin, being the accumulation of calcareous material deposited in drainage basins. Where seen in Texas it differed materially in character from the aeolianite of Australia, but is certainly clothed with soils very similar to the brown solonized

soils. The reason for characterizing these Australian soils as solonized is chemical, there being a large percentage of sodium present in the exchangeable cations, as shown by Prescott and Piper (1932). Except for generally heavier textured subsoils there is only occasional physical evidence of this solonized character in the soils themselves, probably largely because subsoil structural features are virtually obliterated by the high percentage of lime invariably present. The degree of solonization, if any, of the reddish-brown soils cannot be assessed owing to insufficient chemical data.

In a rather more arid area than that occupied by the brown solonized soils, namely on the Nullarbor Plain which lies in an arid area astride the South and West Australian border, there is an extensive development of red to red-brown soil on Miocene limestone. These soils are shallow and strongly alkaline in reaction. They also occur in areas of the desert loam soils wherever limestone is the parent material and is not occupied by the brownish-grey soils described as being related to rendzina. These red soils with their calcareous association could well be called red calcareous desert soils.

I. *Laterite and associated soils*

As mentioned in the Introduction, Prescott, following David (1887), Simpson (1912), and Woolnough (1918) early recognized the ironstone gravel and concretionary masses of certain soils very prevalent in the south-west of Western Australia as being laterite. He also showed that the laterite was of a relict or fossil character, and subsequent work on similar formations in Queensland by Bryan (1939) and Whitehouse (1940) have shown that the laterite is most probably of Pliocene age. In southern Australia in those areas where the laterite remains in association with apparently undissected soil the profile in its A horizon has the morphology of podzolic soils, and there are B and C horizons of mottled clay and kaolinized parent material beneath. These features have led to the soils being termed residual or lateritic podzols, it being recognized that they were formed in association with a peneplain landscape with a seasonally fluctuating water-table. These soils, truncated in varying degrees, are common in southern Australia, important occurrences outside Western Australia being Kangaroo Island, southern Eyre Peninsula and the Mount Lofty ranges in South Australia, the Dundas tableland and Bendigo district in Victoria, Jervis Bay and other small occurrences through to the Australian capital territory in New South Wales, and the Launceston Tertiary basin in Tasmania.

As described in the work of Bryan and Whitehouse, occurrences of laterite in Queensland appear to have been associated with ancient red earth soils which, like the lateritic podzols of southern Australia, have since been dissected. Stewart (1947) has recently described both lateritic red earths and lateritic podzols from the Darwin-Katherine region of the Northern Territory. Secondary siliceous material is commonly found in association with lateritic soils in these more northerly areas. It is uncommon in the southern areas of lateritic podzols, but has definitely been found at Borden in Western Australia, Echunga and Christies

Beach in South Australia, and at Coleraine in Victoria. This siliceous material is commonly known as 'grey billy', and if its presence can be taken as an indication of the former occurrence of laterite, then, taken in conjunction with the areas of laterite still extant, it seems there may have been almost a complete cover of Australia by lateritic soil of one sort or another in Pliocene times.

In Queensland there are some very restricted occurrences of laterite in areas of red loams. These appear to be identical with the soils of the Sudan described by Greene (1945), and certainly the evidence at Toowomba and Childers of formation, under conditions of a rolling topography and water relations involving considerable lateral movement, of the iron- and aluminium-bearing solutions necessary for the formation of laterite, parallels very closely the conditions described by him.

To distinguish lateritic soils from red loams and red and yellow podzolic soils, United States workers normally refer to soils containing laterite, as defined by Buchanan, as ground-water laterite. However, there are soils containing laterite and related formations in the United States. Pendleton (1941) remarks that the actual physical character of laterite, nodular, pisolitic, vesicular, or massive, depends on the nature of the soil horizon in which it is formed, and this observation agrees with Australian experience where the several forms are found in association with various types of soil horizons and include a massive form found in the Hunter Valley of New South Wales formed not in soil but in porous sandstone rock. A similar formation to this was observed near Salina, Kansas, U.S.A., where the flat-topped hills are capped with a massive ferruginous formation of the Dakota sandstone beneath which kaolinization has taken place to considerable depths. In Australia (Stephens, 1946) not only has the massive ferruginized material given rise to soils, but the bevelled dissection has exposed the kaolin which has become the parent material of the soils found on the slopes. Laterite was also seen in Texas in association with the Kirvin gravelly sandy loam, a red podzolic soil with great masses of laterite in adjacent residual areas, and in the Bowie fine sand, a yellow podzolic soil with the laterite and underlying mottled zone and kaolin horizons occurring at a depth of about 10 ft. from the surface.

Taking together the observations on laterite in Australia with those by Pendleton (1941) and Thorp (1940) in Asia, Greene (1945) in Africa, and other workers elsewhere, it would appear that laterite can be expected to occur in various horizons and at various depths in podzol-like, red podzolic, yellow podzolic, and red loam soils. It may be associated with a fluctuating water-table or be of a relict or fossil character now dissected and abandoned by its former water-table, in which case both the laterite and its associated kaolinitic horizons can be subjected to a new cycle of soil formation.

3. *Genetic Relationships*

In the previous section it has been shown that within what may be termed the Great Soil Group spectrum there are varying degrees of difference in the component soils in the different continents. These

differences may be in minor morphological features or involve the whole profile or, again, may be associated with soils for which there is no recognizable counterpart in the other continents. The most notable of these differences and the genetic factors with which they appear to be correlated are summarized below.

(*a*) There is a pronounced difference between the character of the organic A horizons of Australian podzols and podzolic soils and of those of North America and Europe. This is readily seen to be a phytogenetic reflection of the role of the very singular sclerophyll Australian vegetation and the utilization of the debris derived therefrom by a high soil-insect population dominated largely by ants and termites rather than earthworms. The morphological differences attributed to these features could well be termed the Australian phytomorphic deviation of the podzols and podzolic soils.

(*b*) Despite an otherwise similar morphology there is a difference in the nature of the surface horizons of the black earths and chernozems. This difference parallels very closely the similar difference in the red-brown earths and brown earths in Australia and their North American counterparts the reddish-chestnut and chestnut soils and resembles the difference between the reddish-brown and brown soils. Chernozems alone appear to be found in Europe, and, with the probable exception of Tasmania, black earths only in Australia. The black soils of North America have been termed chernozem, and for northern areas this nomenclature appears appropriate, but in southern areas such soils as the Houston clay appear, in surface features such as organic-matter content and structural character, to be nearer the black earth category. The distribution of these various soils when compared with climatic-index and temperature maps points clearly to a relationship with temperature, the chernozem being found in cooler and black earths in warmer areas, and is doubtless a simple reflection of the established relationship between organic-matter content of soils and temperature (Jenny, 1941).

(*c*) There is a difference in general morphology, but particularly in colour, between the chestnut soils of Russia on the one hand and the chestnut and reddish-chestnut soils of North America and the red-brown earths and brown earths of Australia on the other. The genetic factors associated with this difference, particularly between the chestnut soils of North America and Russia, are not apparent.

(*d*) There is a difference in morphology, more particularly in colour, between the soils of the arid areas of the three continents. The presence of grey desert or sierozem soils in North America and Russia and their absence in Australia, and the presence of red desert soils in North America and Australia and their absence in Russia, are in accordance with the presence or absence of suitable climatic zones of cool or hot desert. The discrepancy in colour between the Australian and North American red desert soils is associated with a difference in geomorphology, the genetic history and character of the soils being influenced by the age of the different landscape features with which they are associated. The Australian desert surface is largely composed of relict Pliocene

tableland features and post-Pleistocene alluvial plains. The North American desert appears to be dominated by terraces of Pleistocene age correlated with the different glacial and pluvial periods and low-level alluvial plains of recent age. The light colour of the soils there may thus be a reflection of senescent soils on the terraces and juvenile soils of the alluvial areas, old surfaces with corresponding soils inheriting some morphological characteristics from previous climates.

In the three continents there is a pronounced difference in the presence of different groups of soils in the middle portion of the Great Soil Group spectrum. In Europe there appears to be a normal change from podzol to chernozem to chestnut soils to sierozem. In North America prairie soils are interposed between podzolic soils and chernozem, and brown and reddish-brown soils between the chestnut and reddish-chestnut soils on the one hand and the desert soils on the other. In Australia grey and brown soils of heavy texture, brown soils of light texture, and brown solonized soils are interposed between the red-brown earths and the desert soils. The presence of these soils and their relationship to the hydrologic and geologic factors suggest that the Great Soil Groups in the middle part of the soil spectrum are less stable than the soils associated with the definitely humid or arid areas; that is, genetic factors appear to be more delicately balanced both in relation to each other and to the soil.

In addition, in Australia there is a widespread occurrence of fossil Pliocene lateritic soils in the zone of podzols and podzolic soils that persists to some degree into the sub-humid and arid areas.

These examples may be regarded as instances of hydromorphic, calcimorphic, and chronomorphic deviations within the soil spectra of North America and Australia.

Although calcimorphic soils have long been regarded as intrazonal in character they have, particularly when considered over the full range of morphological features, well-marked zonal relationships. These are rather broader than with non-calcimorphic soils. The following arrangement (Table 1) shows the relationships of calcimorphic soils to climatic

TABLE 1

Parent material	*Climate*			
	Humid	*Sub-humid*	*Semi-arid*	*Arid*
Soft or powdery calcareous material	Rendzina		Grey calcareous soils	Brownish-grey calcareous desert soils
Hard or nodular calcareous material	Brown forest soils	Terra rossa	Brown soils, reddish-brown soils, solonized brown soils	Red calcareous desert soils

features and parent material and is based not only on terra rossa, rendzina, and brown forest soils, but also on calcimorphic soils found in the semi-arid to arid parts of Australia and North America.

Soils on normal, calcareous, or ferruginous parent material are, of course, considerably modified in those situations where hydrogenetic

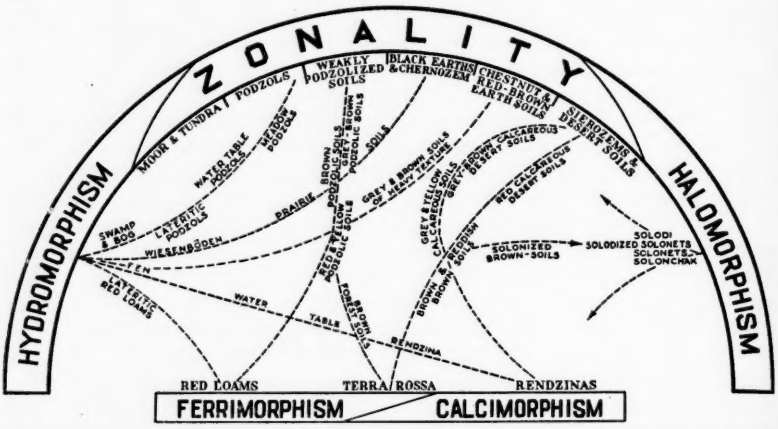

FIG. 3. A taxonomic arrangement of soils showing how they are the expression of varying degrees of automorphism (zonality), hydromorphism, halomorphism, calcimorphism, and ferrimorphism.

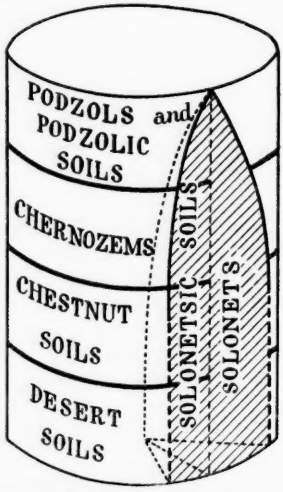

FIG. 4. A diagram showing the occurrence of solonets and solonetsic soils across the main phylum of zonal soils. Decreasing incidence in the podzol and podzolic soil zone and the tendency for halomorphism to become zonal in the desert soils is indicated.

factors operate. Fig. 3 shows the interrelationships of all soils influenced by varying degrees of hydromorphism, halomorphism, ferrimorphism, and calcimorphism. This diagram shows the relationship of these soils to the so-called zonal soils.

Another diagrammatic method of showing the incidence of individual genetic factors is illustrated for solonets and solonetsic soils in Fig. 4.

This figure, devised during discussions with W. G. Harper of the United States Soil Survey, shows clearly how some of the soil categories lie across the main phylum of zonal soils and the method of distinction between soils of full morphological development and those of incipient development as exemplified by solonets and solonetsic members of other soil groups.

The same type of diagram can be used for hydromorphic, skeletal, and largely undifferentiated alluvial-soil categories.

4. *Classification*

In systematizing the data on which the previous sections are based it has not been found necessary to depart either from the categories I to VI set up by Thorp and Baldwin (1938) for Soil Types, Series, Families, Great Soil Groups, Sub-orders, and Orders, or from the morphological basis of classification of categories I, II, III, IV, and VI. In the case of IV, the Great Soil Groups, the morphological basis, especially as expressed by colour, has been retained, but a rearrangement of the subdivisions has been made with the object of showing hydromorphic and other special soils in proper relationship to the automorphic soils of category IV and all in relationship to the new subdivisions of category V. Here the Sub-orders have been changed from an environmental, genetic, and geographical basis to a morphological one founded on the inter-related properties of acidity-alkalinity, clay distribution, and the presence of $CaCO_3$ or $CaSO_4$ in the profile. The Orders of category VI have been retained in Marbut's original form, Pedalfers and Pedocals, with provision for recognition of some overlap between the two.

Using the above arrangement, Table 2 shows the comparative taxonomy of the Great Soil Groups as recognized and mapped on a continental scale in North America, Europe, and Australia. Occurrence is shown in IVA and IVB by appropriate letters (A., E., and N.A.), and identity, where nomenclature is different, by position on the same line under IVA; and IVB shows occurrence but not identity or otherwise of the hydromorphic soils. From the earlier sections and from Table 2 it is apparent that despite resemblances the Great Soil Group spectrum in each of the continents is not identical, there being significant differences in morphology of closely related Great Soil Groups and some geographical expression of Groups in one of the continents and not in the others. These differences are but a decreasing continuation of those expressed in the Type, Series, and Family categories. For complete continental identity we must look to category V, and the morphological basis of the system presented here enables such identity to be stated with some confidence. There is consequently a strong case for naming the Sub-orders, and two alternatives are proposed here, the first following suggestions by Australian colleagues based on the names of eminent soil scientists, and the second on soil properties and hence with some mnemonic value. The first, starting with the acid organic soils, comprises Dokuchaievian, Glinkian, Marbutian, Robinsonian, Prescottian, Kelloggian, and Gautierian. The second, and perhaps preferable, suggestion comprises Organosols, Minorganosols, Sesquiminosols, Sesquisols, Melanosols, Calcisols, and Aridisols.

TABLE 2

A Comparative Taxonomic Arrangement of the Soils of Australia, North America, and Europe

VI. *Order*	V. *Sub-order*	IV. *Great Soil Groups*	
		(A) *Automorphic, calcimorphic, and ferrimorphic*	(B) *Hydromorphic*
PEDALFERS	Acid organic soils	High Moor Soils (E. & A.), Tundra (N.A. & E.) Button Grass Plain Soils (A.)	
	Acid soils with organic and sesquioxide illuvial horizons	Podzols (E., N.A., & A.), Humus Podzols (A. & E.)	Slight: Meadow Podzols (E., A., & N.A.) Moderate: Ground-water Podzols (E., A., & N.A.), Residual Lateritic Podzols and Sandplain* (A.)
	Acid soils with sesquioxide illuvial horizons	Podzols (A. & E.) Brown podzolic soils (E. & N.A.) Grey-brown Podzolic Soils (N.A.) } Weakly podzolized Red and Yellow Podzolic Soils (N.A.) } soils (E.)	Full: Swamp (E., A.), Bog, and Half-Bog (N.A.)
	Acid to neutral soils with sesquioxide eluvial and illuvial horizons	Red Loams (A.), Kraznozems (E.), Laterites (N.A.) Brown Forest Soils (N.A.), Braunerde (E.) Terra Rossa (E., N.A., & A.)	Moderate: Residual Lateritic Red Earth* and Lateritic Red Loams (A.)
PEDOCALS	Soils largely with neutral organic eluvial and neutral or calcareous illuvial horizons	Grey wooded soils (N.A.), Degraded chernozems (E.) Rendzina (E., A., & N.A.) Black Earths (A.) Chernozem (E., A., & N.A.)	Slight: Prairie Soils (N.A.) Moderate: Water-table Rendzina (N.A., E., A.) Full: *Wiesenböden* (N.A. & E.), Fen (E. & A.)
	Soils with neutral eluvial and calcareous illuvial horizons	Red-brown and Brown Earths (A.), Chestnut and Reddish Chestnut Soils (N.A.) Chestnut Soils (E.) Brown and Reddish-Brown Soils (N.A.) Solonized Brown Soils (A.) Brown Soils of Light Texture (A.)*	Slight: Grey and Brown Soils of Heavy Texture (A.)
	Soils with neutral to alkaline eluvial and calcareous and gypseous illuvial horizons —deflated to variable degrees	Grey Desert Soils (N.A.), Sierozems (E.) Desert Loams (A.) Alkaline Brown Soils (E.) Red Desert Soils (N.A.) Stony Desert (A.) Desert Sandhills (A.)	Moderate: (Residual) Desert Sandplain (A.)*

* Chronomorphic

TABLE 3

A Taxonomic Arrangement of Great Soil Group Members (Category IV) recognized in Australia

Automorphic	*Hydromorphic*	*Calcimorphic*	*Ferrimorphic*	*Halomorphic*	*Chronomorphic*
High Moor Peats	..	..	..	..	..
Moor Podzol Peats	..	..	..	..	..
Humus Podzols	Ground-water Podzols and Swamps	..	..	..	
Podzols Grey-brown Podzolic Soils Brown Podzolic Soils Yellow Podzolic Soils Red Podzolic Soils	Meadow Podzols and Swamps	..	..	..	Residual Lateritic Podzols
..	Lateritic Red Loams	..	Red Loams	..	Residual Lateritic Red Earths
..	Ground-water Rendzina and Fen	Terra Rossa Rendzinas	..	..	..
				Solonets Solonchak Solod	
Chernozem Black Earth Brown Earths Red-brown Earths	Grey and Brown Soils of Heavy Texture	..	..	..	..
..	..	Brown Solonized Soils Grey Calcareous Soils	..	..	..
..	..	..	..	..	Brown Soils of Light Texture
..	..	Red Calcareous Desert Soils Grey-brown Calcareous Desert Soils	..	..	..
Desert Loams	..	..	..	..	..
Stony Desert	..	..	..	..	..
Desert Sandhills	..	..	..	..	..
..	..	..	..	..	Desert Sand-plain

On the basis of identifications made on detailed soil surveys and arising from comparisons made in North America and Europe and on the basis of separations within the arid soils such as desert loams, a taxonomic arrangement of soils recognized so far in Australia is presented in Table 3. This with its subdivisions into automorphic, hydromorphic, and other sections is a detailed tabulation of category IV and presents a classification of soils suitable, with any additions found necessary, for mapping the soils of Australia on a continental scale.

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SOME CONSIDERATIONS ON SOIL CLASSIFICATION

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ONE of the most important branches of pedology is that of classification. Many systems have been proposed and many more are possible. All must be subjected to criticism, and the purpose of the present paper is to examine some of the underlying assumptions with a view to attaining greater precision of thought and definition.

In the first place, we must decide what is to be classified. There is now fairly general agreement that the unit of classification is the soil profile; but some divergence is possible in defining its lower limit. Some pedologists would confine the soil profile or solum to the A and B horizons and include the C horizon only for completeness of description. Certainly, if soil-profile characters are to be related to plant growth, the C horizon cannot be left out of account. Unfortunately, it is not always possible to decide where the soil horizons end and where the parent material begins. The A and B horizons, whilst clearly discernible in podzols, are very indefinite in soils of the brown-earth or grey-brown podzolic type, particularly after age-long agricultural use. And thus whilst in most British agricultural soils the material at, say, 6 ft. in depth would generally be regarded as of C character, the level at which it passes upwards into the soil horizons proper is a matter for conjecture.

Some progress might be made in the delimitation of the soil profile by the development of suitable chemical or biochemical methods of examination. For example, the content of active iron compounds, the content of humus, or the numbers of micro-organisms might be used to distinguish the soil horizons from the parent material.

The problem of defining the material to be classified is, however, of less difficulty than that of the philosophical basis of classification. Here one may distinguish between practical and scientific systems. By a practical system one understands a classification based on the expression of some factor or factors known to be of importance in practice. An example of a practical classification is a classification in terms of soils of high, medium, and low lime status. Such a classification presupposes that lime status can be determined quantitatively and that there is a fund of experience enabling the assignment of soils to one of the three categories arbitrarily set up. Similarly, soils might be classified in terms of their known behaviour under tillage or their capacity for retaining moisture.

A scientific (or philosophical) classification is different. It recognizes that soils have many properties, some of which are associated in an apparently causal relationship. For example, the property of texture appears to have a close relationship with mechanical composition; moisture-holding capacity, however defined, is closely related to clay and organic-matter content; whilst the character and distribution of the colloidal material are expressed, amongst other ways, in soil colour.

Just as individual animals and plants are recognized and even defined by a few of their properties, so are individual soils. It is always assumed that individuals agreeing in common possession of a few properties will also agree in the possession of other properties. The greater the number of properties possessed in common, the more confidently can this assumption be made.

In the literature of pedology a number of terms purporting to denote soil classes are widely current, e.g. podzol, laterite, chernozem, rendzina. When a soil is called a laterite it should imply that it possesses a number of characters that are commonly agreed to belong to laterites. Conversely, where a soil is found to possess these characters it is assumed to be a laterite. So far so good, but the conception of laterite becomes blurred when a world view of laterites is attempted. Buchanan in 1807 described a material in southern India as laterite, and if the principle of priority is admitted the term should be restricted to materials having the same properties as Buchanan's laterite. Yet the term has been used to denote materials agreeing with the original laterite only in certain respects and has been extended to denote soil profiles in which certain horizons are considered to be identical or similar to the material described by Buchanan. In the already copious literature there are many definitions of laterite, some of which might even exclude the material to which Buchanan originally applied the term laterite.

In most, if not all, existing systems of soil classification there is a basic assumption that there are individual soils, just as there are individual animals and individual plants. This assumption cannot go unexamined, and in this connexion the attempts made by certain students of soil, notably by H. Jenny, to relate soil properties to soil-forming factors must be borne in mind. Jenny would see the soils of the world not as a universe of individuals but as a kind of continuum varying from place to place in reflection of the varying operations of the factors parent material, climate, &c. The soil at a given point is thus not an individual, but represents a point on a number of curves or sequences. If this is true, then a soil map showing a pattern of soil classes separated by firm boundaries cannot correspond with physical fact.

Those who have actually engaged in soil mapping will be only too well aware of the limitations of soil maps. Generally speaking, the classes are defined by reference to examples at places where the soil class is judged to be typical. Yet a large proportion of the area of most maps is occupied by soil which, if not actually transitional, cannot be regarded as wholly typical. The boundary between one class and another is often a matter of personal judgement, and an area shown on a map as uniform may in fact include a considerable variety of soils. Indeed, the surveyor may be attempting the impossible when he tries to represent the soils of an area by a limited number of categories. The pattern may be rather like that of a picture where uniform patches of colour and sharp boundaries are the exception rather than the rule.

Yet there are also in nature numerous instances of sharp boundaries that can be defined quite objectively, often within a few feet. Equally, there is a large proportion of the area of most countries covered by soils

that vary but slightly. This may be due to uniformity of climate, topography, and parent material.

Many attempts have been made to reduce the soils of the world to an ordered system such as those used in classifying animals and plants. It must be remembered, however, that a soil, even if it can be regarded as an individual, is entirely passive, whereas a plant or an animal, even although greatly modifiable by environmental factors, has its own particular response depending on its genetic structure. The proportion of individual plants or animals that can be regarded as transitional is exceedingly small, whilst in soils it may comprise the majority of the soils of a given area.

The existence of a considerable proportion of transitional soils should not, in itself, prevent us from recognizing or attempting to recognize soil classes or species. Indeed, the fact that soil names are used would appear to show that classes or species do exist. If every soil was merely a point in a succession or system of successions it would hardly provoke the observer to give it a class name.

We must now inquire into the significance of the class names applied to soils. There are at present many class names in current use, and it is not invariably the case that a given name such as podzol is always used with the same significance. It is, perhaps, a counsel of perfection, but no writer should use a term unless (*a*) he himself knows precisely what it connotes, and (*b*) he is quite sure that reasonably instructed readers understand it in that sense.

When we look at a soil profile we perceive certain facts and, if sufficiently informed in pedology, say this is a laterite or this is a podzol. We perceive the particular example; but in speaking or thinking of any podzol, we are using the word 'podzol' as a counter or symbol to denote all podzols.

In order to clarify our thinking, it may be helpful to consider briefly how ideas are presented to and exist in our minds. How is it that we are able to think and reason about things in their absence? We may, of course, conjure up mental images, but such a method of thinking would limit us narrowly. Thus, it might be easy to think of a square or a triangle by conjuring up a mental image, but although it is possible to think and reason about a figure of ten thousand sides, no mental image of it could be formed. The objects known by sensation or as mental images are *particulars*, the objects about which we think and reason are *non-particulars*. Some would say that these non-particulars about which we think and reason are *concepts*; others would call them *universals*. The traditional meaning of a universal is an idea which is either antecedent to particulars or else abstracted by the mind from particulars. In practice, it appears that *concept* and *universal* are used almost synonymously, but a useful distinction can be drawn between (*a*) universals or concepts that are observed because they are either antecedent to or existing in the particulars, and (*b*) universals that are mental constructions from particulars. An instance of the former is the redness of red objects; an instance of the latter is the arbitrary first-classness in an examination list or the high lime status postulated of certain soils.

What is the relationship between particulars and universals? Broadly speaking, there are three ways in which this problem has been approached, namely, (*a*) Realism; (*b*) Aristotelian-Thomist Realism; and (*c*) Representationist theories, notably Nominalism, Imagism, and Conceptualism.

In Realism, *sensu stricto*, as originally propounded by Plato and developed by St. Augustine, the only realities are universals whilst particulars are merely phenomena. The common elements by which we recognize particulars, e.g. podzols, are entities subsisting in the supra-sensible world. This is, to the Platonist, the real world, revealed to us imperfectly through the perceptions of sense. Realism of this type dominated Western thought until the eleventh century.

Although Realism may seem repugnant to the twentieth-century scientist, many pedologists appear to be unconscious Realists in their attitude to soil species. Thus, when a pedologist discusses the question whether a particular soil is or is not a podzol he is tacitly assuming that there is an ideal podzol, of which the particular profile may or may not be an instance. Attempts to *discover* the essential characteristics of a podzol imply a Realist position.

Developed from the extreme Realism of Plato and St. Augustine is the moderate Realism of Aristotle and St. Thomas Aquinas. According to this view, universals do exist, but are implicit in the particular instances and elicited by the human intellect. The podzol character is found in all instances of podzols but has no existence apart from them. Neither does it exist in the mind, but is abstracted by the mind through observation of the particular instances. Such a theory would appear to be satisfactory, provided the supposed classes really exist. For example, it would be valid as applied to the abstraction of a universal *Ranunculus repens* from observed instances, but it is not so clearly applicable to podzols, for we may be mistaken in supposing that such a class exists independently of our own mental construction.

Contrasted with the Realist philosophies are the Representationist philosophies, of which the chief examples are Nominalism, Conceptualism, and Imagism, which dispense with the assumption of universals and regard the terms used in our thinking as essentially symbolic. But whereas the Nominalist regards the words themselves as symbols directly mediating to the mind the extra-mental reality, the Conceptualist interposes between the word and the object an intra-mental idea or concept, arbitrarily framed for a particular purpose by abstraction from particular impressions, and the Imagist similarly interposes an image or images of the absent object.

Let us now attempt to illustrate these positions by reference to soil classes and see what is meant by the statement that a given soil is a podzol (or laterite, or chernozem, &c.).

The Augustinian Realist means that this soil is a particular instance of an ideal podzol, a podzol, so to speak, 'laid up in heaven'. Behind all the sensible impressions that we receive, e.g. the raw humus layer, the bleached A_2 horizon, there is the idea of podzolness of which these characters are merely external manifestations.

The Aristotelian-Thomist Realist maintains also that there is an ideal or universal podzol, but that it is something inherent in the class and elicited or abstracted by the human mind. Whilst the Augustinian might hold that the ideal podzol exists even if no particular instances were observed, the Thomist would deny this and regard the universal podzol as inherent in the particular instances. Classes are *given*, and are perceivable, but they are not made by the perceiver.

Coming to the Representationists, one can say at once that, on the Imagist theory, the statement that a certain soil is a podzol merely means that the soil evokes a mental image of a podzol, which must be a particular podzol.

The Nominalist would say that podzol is merely a name of a class of objects resembling a standard object to a required degree. It is difficult to see how the Nominalist can avoid postulating a universal if he admits the existence of classes, but he would say that the resemblance between members of a class is something ultimate, something that just happens, in the same way that a number of candidates happen to get over 70 per cent. marks and are called Class I.

The Conceptualist would also deny the existence of a podzol universal, but would say that by selecting certain characters he can define a class to which he gives the name podzol. Whilst the Realist would say that classes are given, the Conceptualist, although recognizing classes, would say that they are of his own making. He selects certain characters and by them defines his podzol. He might equally have selected another ensemble of characteristics and defined soils suitable for the growth of barley. But is there not also something given in the list of attributes by which a class is defined? The ensemble of characteristics is one that is actually observed to occur. The observer is not free to choose any ensemble, for then he might set up classes that might in practice have no members.

The positions outlined above appear to be distinguished mainly in that the Realists would postulate a universal inherent in or antecedent to the idea of podzol whilst the Representationists would hold that the idea of a podzol is a construction of the mind and does not exist independently of the mind. If it is a universal it is a constructed universal.

The Realist would draw a distinction between the thing itself, e.g. the podzol, and the complex of characteristics by which we are aware of it, and, according to R. I. Aaron, our knowledge of universals may proceed through an initial awareness of the thing itself, i.e. table, man, bed, to an awareness of the characteristics that form the complex. We cannot, therefore, assume that universals are always abstractable from observed characteristics, still less are they always mere complexes of qualities and relations.

Now whether the universal podzol can be taken in a Realist sense and be conceived as existing separately from its observed characteristics or whether it is merely a complex of observed or observable qualities or relations is the central problem of this discussion. The writer ventures to think, perhaps mistakenly, that the idea of a podzol, if it is a universal, is a constructed universal. The complex of characteristics that make up

the concept can only be a creation of the pedologist: yet not an entirely arbitrary creation, for a certain ensemble of properties is given and does, with certain variations, occur in nature.

This discussion is intended merely to draw attention to the possible implications of using certain terms in classification. At present a number of terms are in common use and it is unlikely that a given term, e.g. podzol, is always used in the same sense. It may even be that individual authors themselves may not be quite clear as to the precise meaning they attach to their terms. If, as the writer holds, the terms in use represent not real universals like the species and genera of animals and plants, but complexes of characteristics or constructed universals, then it is of the highest importance that co-operative effort should be directed towards definition. The object of such effort would be to construct a glossary of terms. A beginning might well be made with some of the commoner terms, including podzol, chernozem, gley, rendzina, &c. Even if the classes recognized by the pedologist are real universals, it is equally necessary to list the characteristics by which they may be recognized.

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SOME OBSERVATIONS ON THE CLASSIFICATION OF SOIL TYPES

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THE discrimination of soil types within a series is based chiefly on variations in texture, but there appear to be no published quantitative measurements of this variation, nor indications of the requirements to be fulfilled before a series is subdivided into types. It has seemed desirable, therefore, to obtain some definite values for the variation occurring in an area of limestone soils surveyed for another purpose. These results are considered from a statistical aspect and what is thought to be a more rational approach to the definition of soil types is presented.

Area Surveyed

The soils of an area of 200 square miles of the Cotswold Hills, mostly lying to the north and west of Burford, Oxon., were mapped by transect surveying by C. G. T. Morison and Mrs. Wright in connexion with another problem (to be published). From among the soils recorded two shallow skeletal brash soils were selected for intensive sampling; they belong to the same unnamed soil series and were derived from two Jurassic limestone formations—the Great and Inferior Oolites, respectively. Within the survey area the occurrence of the two rocks and their derived soils is topographically similar. The country is undulating and ranges in altitude from 275 to 880 ft., most of the higher ground being capped with Forest Marble (G 6), Great Oolite (G 7), or Inferior Oolite (G 5): there is Lower Lias clay (G 1) in the valley bottoms and a considerable amount of alluvium. Most of the land is arable. The formations present were identified from H.M. Geological Survey 1-in. maps.

Sampling and Analyses

Twenty sampling sites were allocated at random on shallow brash soils (defined as 6–15-in. auger penetration) overlying Inferior Oolite, and the same number on the Great Oolite: at each site two profile pits were dug 30 yards apart and the plough layer sampled. Profile descriptions were made and, subsequently, laboratory determinations of pH, calcium carbonate, and mechanical analysis were carried out on the samples. A calomel-glass electrode pH meter was used in three ways for pH measurements: in one method the fresh moist soil was packed around the glass electrode and the cell completed by pressing an agar-KCl bridge into the soil. The fresh soil was also used to prepare an approximately 1 : 2½ soil : distilled water suspension, the pH of which was measured in the usual way after 2 minutes' stirring, and, finally, the air-dry fine earth was used to prepare a 1 : 2 soil : water suspension whose pH was measured ½ hour after mixing.

Calcium carbonate was estimated by gravimetric determination of the carbon dioxide evolved from the fine earth on treatment with acid. Mechanical analyses were made by means of sieves and decantation, if

necessary after the removal of carbonates with dilute acid. The percentages of the insoluble residues were recalculated to add up to 100 per cent. to be comparable with one another: expressed in this way they represent the textures of the insoluble residues, but may have little connexion with the field textures of the original soils.

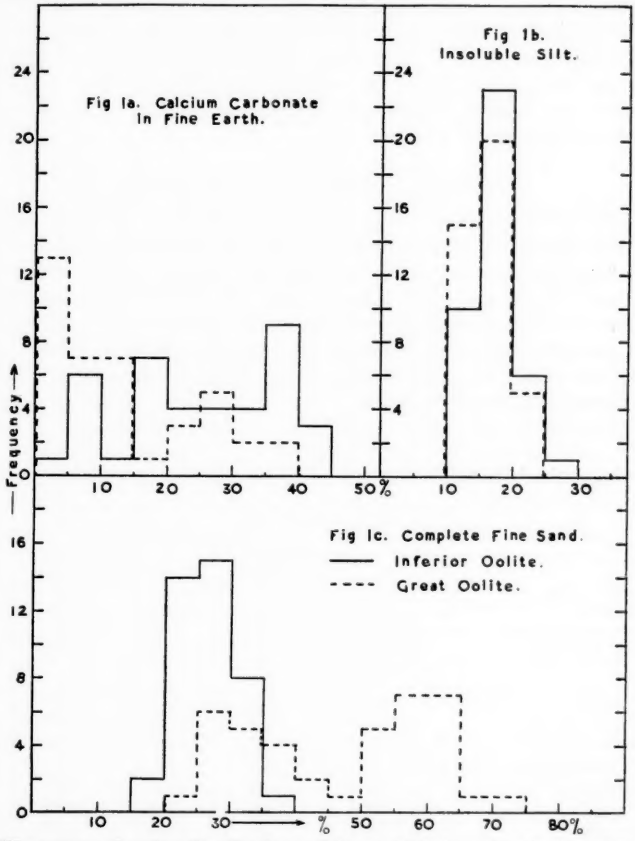

FIG. 1. Histograms showing distributions of the analytical results of selected fractions.

Experimental Results

Comparison of the results from the pairs of pits at each sampling site showed that the variation between the two pits at one site was much smaller than between different sites. This is in agreement with the results of Youden and Mehlich (1937), who found that variation between pits less than 100 ft. apart was negligible. To avoid underestimating the variation for statistical purposes the mean of the two samples from each site was used: this gave two lots of 20 figures for each analytical determination. The histograms (Fig. 1) were plotted from the data of the original 40 samples for each soil.

The two rocks from which these two soils are derived are similar in appearance, composition, and behaviour on weathering. The soils themselves differ little; an analysis of the profile descriptions made in the field indicated that some of those from the Great Oolite were slightly heavier in texture and a richer brown in colour than those from the Inferior Oolite, but it would be impossible to distinguish with certainty in the field between these two soils without knowing from which rocks they were derived. They have, however, been treated in the first instance as two different soil types on the basis of their lithological origin, and the validity of this assumption is considered in the light of the results of statistical analysis.

Discussion: Definition of Soil Types

In Table 1 the results are summarized in the form of their means and standard deviations. The *t*-test was applied to discover which properties showed significant differences between the Great and Inferior Oolite soils. Four differences conformed to the 5 per cent. level, and of these four, three were greater than the 1 per cent.; however, two of these were estimates of the fine-sand fraction. It was this fraction which showed the most marked difference between the two soils and suggested itself for characterizing the two types.

TABLE 1

Mean Analytical Data of Soils Classified according to Geological Origin

	Inferior Oolite soils		*Great Oolite soils*		
	Mean	*Standard deviation*	*Mean*	*Standard deviation*	*t-test*
pH: fresh soil . . .	7·22	0·378	7·37	0·167	Insig.
pH: fresh soil+water . .	7·88	0·402	8·05	0·148	Insig.
pH: dry soil+water . .	7·84	0·302	7·80	0·113	Insig.
	%	%	%	%	%
Calcium carbonate in fine earth	25·2	11·69	13·3	11·38	1
Complete coarse sand . .	15·7	5·58	10·6	8·17	5
Complete fine sand . .	26·5	4·38	47·0	13·70	1
Insoluble coarse sand . .	5·1	5·90	4·6	5·47	Insig.
Insoluble fine sand . .	29·0	4·38	35·2	7·38	1
Insoluble silt . . .	17·4	2·59	16·0	2·88	Insig.
Insoluble clay . . .	48·5	7·77	44·2	5·83	Insig.
Number of samples . .	20		20		

This raised the question of the definition of soil types and the requirements that should be fulfilled. The following three seem important:

1. If a soil series is subdivided into two or more types, they must be defined in terms of a limiting percentage of one fraction, or possibly a limiting ratio of fractions, e.g.

$$\frac{\text{Sand}}{\text{Silt}+\text{Clay}}.$$

2. The soil types distinguished in this way should be significantly

different in the statistical sense; the level of significance would to some extent depend on the purpose of the survey.

3. It is desirable that the types should be distinguishable in the field by a competent soil surveyor.

These suggestions may be considered in turn.

In applying the first of these requirements to the two Cotswold soils the data for each fraction were plotted as histograms, three of which are shown in Fig. 1. The calcium carbonate in the fine earth (Fig. 1*a*) shows a wide variation in both soils, that in the Great Oolite suggesting a bimodal distribution, but the Inferior Oolite is indefinite. Fig. 1*b* shows distributions with very small standard deviations, but the mean percentages of the two are so similar that they are not significantly different.

The complete fine-sand fractions show the most significant difference, and it was thought that somewhere between the two means, 26·5 and 47·0 per cent., there might lie a point which would conveniently form a limiting value: instead it was discovered that the Great Oolite soils show a clear bimodal distribution, one phase of which is very similar to the Inferior Oolite soils (Fig. 1*c*). This division corresponds to two different phases of the Great Oolite soils in this area of the Cotswolds, but no satisfactory reason can be found in topography that might account for differential sorting of the particles, or in the character of the rock. It is possible that the difference may be due to contamination by glacial drift, since the samples with the higher percentage of fine sand mostly came from the north-east corner of the survey area, and Arkell (1947) indicates that the southernmost boundary of the ice sheet approached closest at this point. The minimum in the bimodal distribution (47 per cent.) forms a convenient natural limit with which to define two soil types: it is an unexpected coincidence that this minimum exactly lies at the mean fine-sand content of the Great Oolite soils. The distribution of Great Oolite soils with less than 47 per cent. complete fine sand is so similar to that of the Inferior Oolite soils that they may be grouped together in one type called the Coarse Sandy soils, while the other type is represented by soils having more than 47 per cent. complete fine sand and referred to as the Fine Sandy soils.

The statistics of these two soils regrouped in this way have been recalculated and are shown in Table 2. That the two groups amalgamated to give the Coarse Sandy soils had very similar population distributions is shown by the small changes that have occurred between the corresponding means and standard deviations in Tables 1 and 2, columns 2 and 3. The Fine Sandy soils show markedly smaller standard deviations for most of the fractions, and when the *t*-test is applied to the two new soil types more of the fractions show significant differences. These two types defined on the basis of the histograms are a better classification of the shallow limestone brash soils in this area of the Cotswolds than was the geological one originally adopted; this grouping fulfils better the second requirement previously propounded for the definition of soil types.

The third requirement—that soil types differentiated on statistical grounds should also be readily distinguishable to a field surveyor—is

TABLE 2

Mean Analytical Data of Soils regrouped into Coarse Sandy and Fine Sandy Soils

	Coarse Sandy soils		*Fine Sandy soils*		
	Mean	*Standard deviation*	*Mean*	*Standard deviation*	*t-test*
	%	%	%	%	%
Calcium carbonate in fine earth	23·4	11·26	8·3	10·49	1
Complete coarse sand . .	15·8	6·20	6·0	5·16	1
Complete fine sand . .	28·8	6·18	57·6	6·58	1
Insoluble coarse sand . .	6·2	6·07	1·4	1·34	5
Insoluble fine sand . .	29·4	4·37	39·2	7·04	1
Insoluble silt . . .	17·1	2·58	15·8	3·24	Insig.
Insoluble clay . . .	47·3	7·20	43·8	6·54	Insig.
Number of samples . .	29		11		

one that is not likely to raise many practical difficulties, but further data are necessary before it can be discussed in more definite terms. Co-operation of experienced field surveyors would be required to discover with what precision it is practical to assign soils to a given texture group and what is the minimum variation in mechanical composition that can be detected with certainty. The sensitivity of the usual touch tests depends on the composition of the soils: for example it is easier to detect a small change in the amount of the clay fraction in a predominately sandy soil than in a heavy soil.

Intensity of Sampling

The mean ($\bar{x}$) obtained from the analyses of a number (n) of samples of a soil type is an estimate of the true or population mean (m). The reliance that may reasonably be placed on this estimate depends upon three factors: the number of samples, the standard deviation of the population, and the magnitude of the mean. Conversely, if the desired accuracy (p) is known, it is possible to calculate how many samples are necessary to be fairly certain that m is within p per cent. of $\bar{x}$, using the following expression (Snedecor, 1946, para. 17.4):

$$n = \frac{(100ts)^2}{p\bar{x}}.$$

In this t may be taken as 2·6. In Table 2 the values of s, the standard deviation, range from 1·34 to 11·26 with a mean of about 6·0; in the absence of more extensive data concerning the standard deviations found among various soil types this value of 6·0 may be used to calculate the number of samples required to obtain results not differing more than 2, 10, and 50 per cent. from the population mean.

The variations of the number of samples with the estimated mean ($\bar{x}$) are shown in Fig. 2 for $p = 2$, 10, and 50 per cent. From these curves it may be seen that many more samples are required to obtain a reliable estimate of a fraction if it constitutes a minor portion of the whole fine earth, than if it is the predominant fraction. On the assumption that

the value of the standard deviation used in these calculations is representative of other soils, it follows from Fig. 2 that 10 samples give an estimate of the mean that can only be trusted to be within 50 per cent. of the population mean if $\bar{x} > 10$ per cent. of fine earth. These figures are only approximate because the data on which they are based is scanty, but they do suggest that it is inadequate to characterize a soil

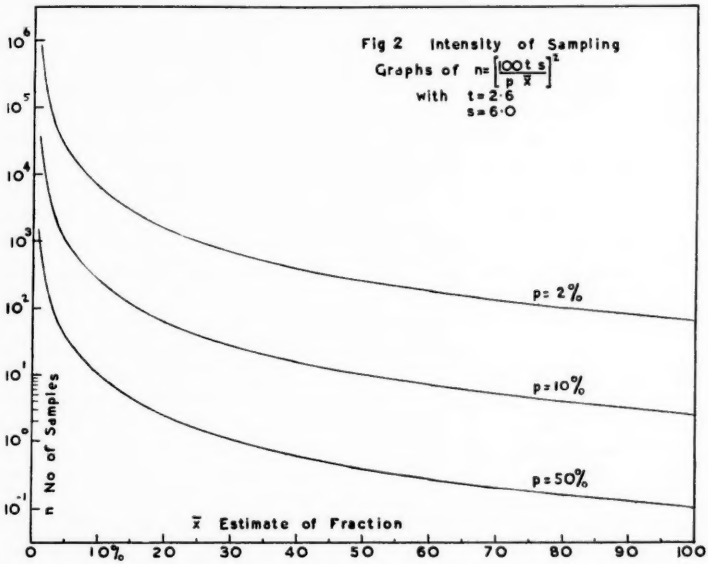

FIG. 2. Intensity of sampling curves showing the number of samples necessary to achieve certain standards of accuracy.

type or soil series by two or three analyses only, unless there is good reason to believe that the soil is very uniform in texture.

Summary

The application of statistical methods to some soil-survey data has been used to illustrate the suggestion that soil types would be more reasonably classified on the basis of histograms, and represented by certain statistics such as the means and standard deviations. The latter are employed to obtain an estimate of the intensity of sampling necessary to achieve certain standards of accuracy in the mean results of a number of soil analyses.

Acknowledgements

I wish to express my gratitude to Mr. C. G. T. Morison, formerly Reader in Soil Science at Oxford University, who supervised my work in his department, to Mr. G. R. Clarke, who guided me in the field work, and to Mr. D. J. Finney (Oxford University) and Dr. B. L. Welch

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A NEW DIAGRAM FOR THE TEXTURAL CLASSIFICATION OF SOILS

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Mechanical Analysis and Particle Size

SUBSEQUENT to the adoption of the international particle size for mechanical analysis, the writer (1937) observed that in certain soils considerable further amounts of fine sand passed through the sieve after drying at 105° C., the amount of fine sand further sieved out increasing as the amount of total sands increased. He quoted an instance where mechanical analysis by the usual wet sieving under a jet of water yielded 8 per cent. fine sand whereas by adding on the residue sieved out after drying the new figure was 29·2 per cent. In view of the possibilities of such discrepancies the writer has always used the dry-sieving technique, which he finds involves very little extra work and, in his opinion, gives a more correct grading of the two sand fractions.

In the official method, stones, &c., retained by a 2-mm. round-hole sieve, are discarded previous to analysis and do not enter into the result. But those who are acquainted with the soil in the field will concede that the 'feel' of a soil is influenced by particles considerably larger than 2 mm. Gravel and fine rubble up to 10 mm. essentially form an integral part of the soil, and cannot rightly be excluded from its mechanical or physical composition. The writer would therefore tentatively offer the following more comprehensive scale, which does not materially diverge from the conventions of the International Society of Soil Science:

Coarse sand and gravel	10–0·2 mm.
(Gravel or grit	10–1·0 mm.)
Fine sand	0·2–0·02 mm.
Silt	0·02–0·002 mm.
Clay	Less than 0·002 mm.

The above grading has been used by the writer for some years, the amount of gravel and grit always being placed in brackets to emphasize that it is already included in the 10–0·2 mm. range.

With regard to the lower limit for gravel being 1·0 mm., which brings it into the international coarse-sand range, the writer has encountered numerous soils in which there is an accumulation of fine concretionary gravel, quite distinct from coarse sand, that readily passes the 2 mm. sieve, but is mostly retained by the 1 mm. sieve. The use of a 1 mm. sieve for gravel is, of course, a reversion in part to the former U.S. Bureau of Soils system, and also the old British system, both of which set the limit for gravel at 1 mm.

For the purposes of the diagram given in this paper the four fractions, inclusive of gravel, are calculated to the basis of 100 per cent.

Diagrammatic Classification

Diagrammatic classification is an attempt to establish a set of permanent reference standards, and to enable standards and conventions established by one group of workers to be related to those of any other group (Prescott, Taylor, and Marshall, 1934). In 1927 Davis and Bennett extended Whitney's (1911) work on texture classes, and produced a triangular diagram based on extensive material obtained by the former U.S. Bureau of Soils. In this triangle, in which sand (2–0·05 mm.), silt (0·05–0·005 mm.), and clay (less than 0·005 mm.) are calculated to 100 per cent., 10 textural groups were arrived at, based, no doubt, on relationships between U.S. survey field descriptions and corresponding mechanical analyses. These 10 classes were further extended to 20 by reference to the triangular diagram and by a further subdivision of the small sand triangle into sands and loamy sands along the 85 per cent. sand margin and, additionally, by prefixing coarse, fine, and very fine to the sand and sandy-loam classes.

Later, Prescott, Taylor, and Marshall prepared a triangle which was based on field observations in Australia, correlated with the large store of American experience available in the diagram of Davis and Bennett. In this way resulted an 'international' triangle into which the older United States triangle had been projected. The writers found the greatest divergence in the clay loams, the American loams and clay loams being much lighter soils than the Australian soils of the same name.

Tommerup (1934) rightly points out that 'one of the urgent needs of the soil surveyor is a code of reference whereby he may describe his field observations on the colour, feel, and appearance of soils in definite terms which are readily linked with more precise measurements made on laboratory samples, and which may be understood by others without actually seeing the soils'. He accordingly drew up a set of 13 texture grades based on international grain sizes, and also provided an equilateral triangle for expressing the principal textures.

Considerable experience in field and laboratory has encouraged the writer to devise a system for obtaining the textural classes using the four fractions coarse sand and gravel, fine sand, silt, and clay. The difficulties of such diagrammatic representation were voiced by Prescott, Taylor, and Marshall who tentatively presented a tetrahedron subdivided to represent a limited number of mechanical analyses of soils.

In view of the inability to turn to field workers in soils for an entirely unanimous verdict on soil textural classes the writer believes it more desirable to evolve a symmetrical diagram, marking off the boundaries of what he considers a fair and practical representation of the limits of soil textural classes. The diagram was evolved through the following stages:

In sketch 1 clay is represented as grading in a linear fashion up to fine sand and, in the equivalent coarser groups, silt is represented as grading up to coarse sand. In sketch 2 the clay-silt combination is represented as grading up to the fine sand-coarse sand combination. A

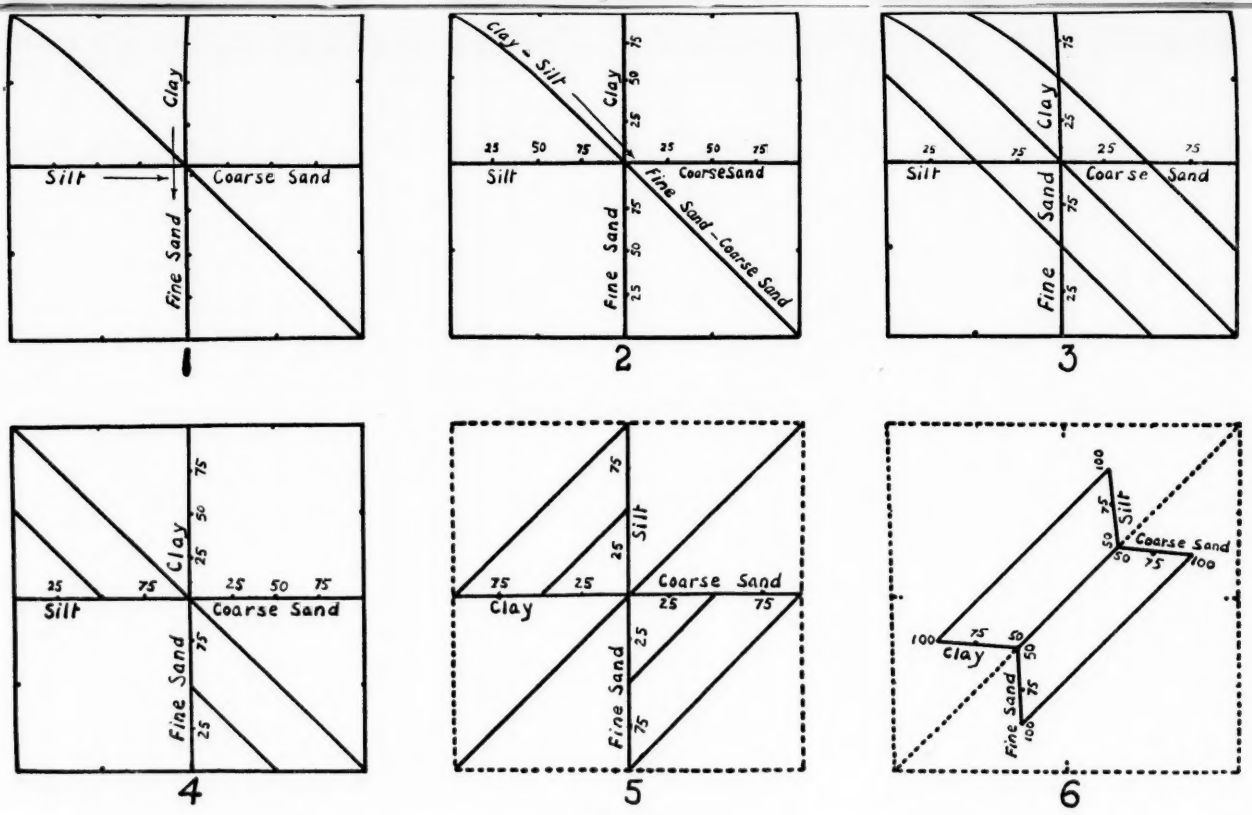
Clay
Silt
Coarse Sand
Fine Sand
1
Clay - Silt
Clay
Silt
Coarse Sand
Fine Sand - Coarse Sand
Fine Sand
2
Clay
Silt
Coarse Sand
Sand
Fine
3
Clay
Silt
Coarse Sand
Fine Sand
4
Silt
Clay
Coarse Sand
Fine Sand
5
Silt
Coarse Sand
Clay
Fine Sand
6

FIG. 1.

50 per cent. combination is selected as the lowest representative amount for the definition of each group, hence 50 per cent. becomes the critical measure for the fractions. In sketch 3 lines are drawn to include only fractions above 50 per cent., and, as it is redundant to have these on either side of the axis, the quantities are now represented as in sketch 4. To unify further the diagram and to enable a reorientation into the clay+silt and fine sand+coarse sand combinations the two groups are now presented as in sketch 5. In sketch 6 the two groups are brought together along a common axis, and a grading from the combined finer fractions to the combined coarser fractions is now represented.

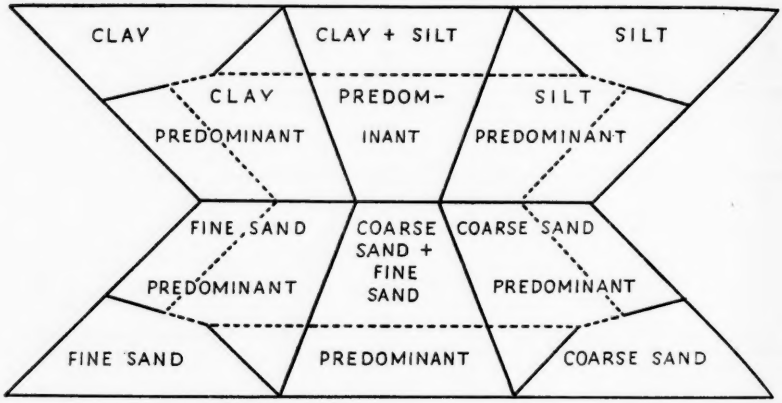

FIG. 2.

In Fig. 2 the area within the diagram is symmetrically subdivided and the areas where each fraction predominates detailed. To obtain the actual boundaries the writer was obliged to call partly upon his own judgement of the common limits of textural soil classes.

In more detailed measure did he apply the same process to obtain the boundaries of the soil classes in the full diagram. Insomuch as he has had to call upon a certain amount of originality at this stage, so may he be criticized. In obtaining his boundaries he was not able to regard clay as 'the principal factor controlling texture', but as a fraction taking its part on the purely physical basis of particle size equally with the other three fractions. The writer's experience with soils has led him to conclude that the sand fraction plays a role just as important as the clay fraction in determining the textural class in the field. He would not regard a soil containing 51 per cent. clay and 49 per cent. total sands as a heavy clay, any more than he would regard it as a sand. In assessing the textural class he makes a mental effort, based on his own experience naturally, to give equal consideration to each of the four fractions he can detect by 'feel' and visual perception. Further than this, and appreciating the great divergence among individual workers, he has favoured a symmetrically equal diagrammatic representation of the four fractions. The delimitation of textural classes was then decided

upon partly by his own experience, endeavouring not to diverge materially from commonly accepted standards of reference. Below is presented such a provisional diagram, illustrating some 32 soil textural classes.

The 32 textural classes were arrived at by computing the various possible combinations, loam being regarded as an hypothetical fraction:

TABLE I

Table for computing Total Number of Soil Classes

	Coarse sand (and gravel)	*Sand*	*Fine sand*	*Loam*	*Silt*	*Clay*
Coarse sand (and gravel)	..	..	..	Coarse sandy loam	Coarse sandy silt	Coarse sandy clay
Sand	..	..	..	Sandy loam	Sandy silt	Sandy clay
Fine sand	..	..	..	Fine sandy loam	Fine sandy silt	Fine sandy clay
Loam	Loamy coarse sand	Loamy sand	Loamy fine sand	..	Loamy silt	Loamy clay
Silt	Silty coarse sand	Silty sand	Silty fine sand	Silty loam	..	Silty clay
Clay	Clayey coarse sand	Clayey sand	Clayey fine sand	Clayey loam	Clayey silt	..

The two classes not appearing in this table are silty clay loam, and clayey silt loam. These two classes originate by postulating a particle size intermediate between silt and clay, or resulting from an averaging of these two states, just as sand is an average between coarse and fine sand. This particle state could best be termed silt-clay or clay-silt, and qualified by the term loam would yield four textural classes, viz. loamy clay-silt, loamy silt-clay, clayey silt loam, and silty clay loam. The latter two commoner textural classes have been adopted.

Border-line cases

Undoubtedly the above diagram will result in much adverse criticism. As regards its possible shortcomings in not being based entirely on field observations, the writer would like to point out that he uses it primarily to assess textural classes from mechanical analyses in the laboratory.

In his experience field observations vary so widely among individuals that a symmetrical diagram would appear to be a better starting-point than an averaging of widely varying observations which can in no way lay claim to exactness, being based on the skill of observers whose judgement is unwittingly liable to considerable errors.

Criticism against the diagram as such may be levelled on two points. Firstly, the confusion arising out of border-line cases ordinarily between textural classes and, secondly, border-line cases along the axis of the diagram.

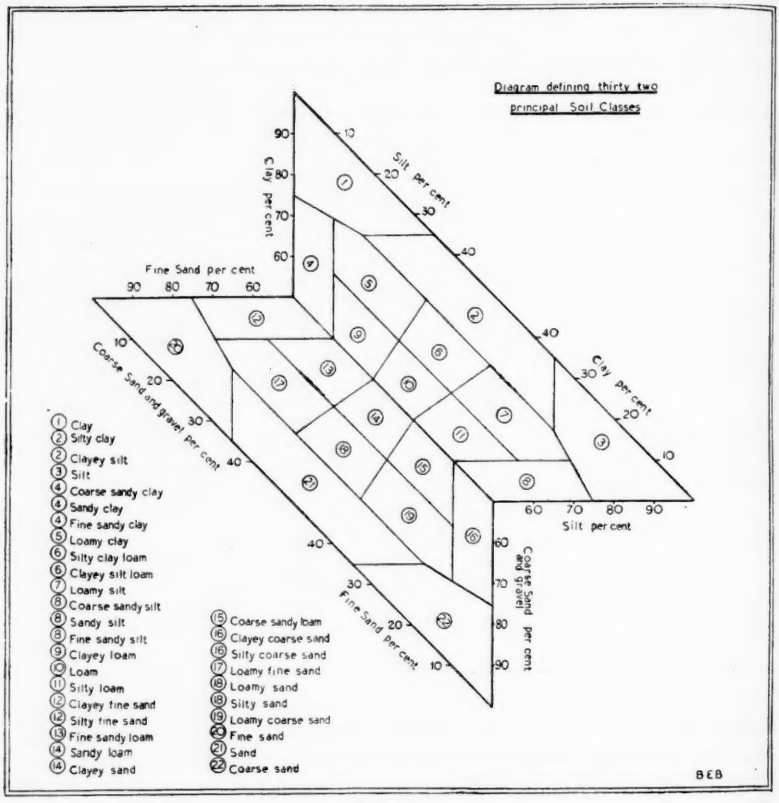

FIG. 3.

In the first instance the individual must use his judgement in the same way as he would with the two-dimensional triangle. In the second case the position is more difficult.

The difficulty arises when the groups (*a*) coarse sand and gravel and find sand, and (*b*) silt and clay each total 50 per cent., and the point lies along the axis. In such cases the higher fraction in either group decides the textural class.

The following examples will serve to illustrate this:

Coarse sand and gravel %	*Fine sand %*	*Silt %*	*Clay %*	*Textural class*
13	37	6	44	Fine sandy clay
9	41	18	32	Clayey fine sand
48	2	25	25	Clayey or silty coarse sand
31	19	42	8	Coarse sandy silt
35	15	0	50	Coarse sandy clay

When, however, in still rarer instances, a similar percentage of single fractions may occur in each group, the textural class is then decided equally by the higher fraction in either group. The following are examples:

Coarse sand and gravel %	*Fine sand* %	*Silt* %	*Clay* %	*Textural class*
33	17	17	33	Coarse sandy loam or clay loam
22	28	22	28	Sandy loam (clayey sand) or loam
43	7	43	7	Silty coarse sand or coarse sandy silt
18	32	32	18	Fine sandy loam or silt loam

Texture Classification Definitions

The following table of limits for 10 groups of the 32 soil classes is arrived at from the diagram, the fraction coarse sand implying coarse sand and gravel. The percentages are given to the nearest whole number:

A. 1. Soils containing not less than 75 per cent. total sands:
Coarse sand
Sand
Fine sand

2. Soils containing not less than 65 per cent. and less than 82 per cent. total sands:
Loamy coarse sand
Loamy sand and silty sand
Loamy fine sand

3. Soils containing not less than 50 per cent. and less than 65 per cent. total sands:
Coarse sandy loam
Sandy loam and clayey sand
Fine sandy loam

4. Soils containing not less than 50 per cent. but less than 79 per cent. total sands:
(*a*) Less than 10 per cent. fine sand:
Silty coarse sand (more silt than clay)
Clayey coarse sand (more clay than silt)
(*b*) Less than 10 per cent. coarse sand:
Silty fine sand (more silt than clay)
Clayey fine sand (more clay than silt)

B. 5. Soils containing not less than 50 per cent. but less than 79 per cent. silt and clay:
(*a*) Less than 10 per cent. silt:
Coarse sandy silt (more coarse sand than fine sand)
Sandy silt
Fine sandy silt (more fine sand than coarse sand)
(*b*) Less than 10 per cent. clay:
Coarse sandy clay (more coarse sand than fine sand)
Sandy clay
Fine sandy clay (more fine sand than coarse sand)

6. Soils containing not less than 50 per cent. and less than 65 per cent. silt and clay:
Silty loam
Loam
Clayey loam

7. Soils containing not less than 65 per cent. and less than 82 per cent. silt and clay:
   - Loamy silt
   - Clayey silt loam (more clay than silt)
   - Silty clay loam (more silt than clay)
   - Loamy clay

8. Soils containing not less than 75 per cent. silt and clay:
   - Silt
   - Clayey silt (more clay than silt)
   - Silty clay (more silt than clay)
   - Clay

The following table presents the ranges of percentages of two qualifying separates in each soil class:

TABLE 2

Percentages of Separates in 32 Soil Classes

Textural class	*Coarse sand and gravel %*	*Fine sand %*	*Silt %*	*Clay %*
Coarse sand	65–100	0–35	..	..
Sand	18–65	18–65	..	..
Fine sand	0–35	65–100	..	..
Loamy coarse sand	40–69	10–33	..	..
Loamy sand	27–49	27–49	..	..
Silty sand	27–49	27–49	..	..
Loamy fine sand	10–33	40–69	..	..
Coarse sandy loam	30–56	10–27	..	..
Sandy loam	20–40	20–40	..	..
Clayey sand	20–40	20–40	..	..
Fine sandy loam	10–27	30–56	..	..
Silty coarse sand	40–75	0–10	..	..
Clayey coarse sand	40–75	0–10	..	..
Silty fine sand.	0–10	40–75	..	..
Clayey fine sand	0–10	40–75	..	..
Coarse sandy silt	..	..	40–75	0–10
Sandy silt	..	..	40–75	0–10
Fine sandy silt	..	..	40–75	0–10
Coarse sandy clay	..	..	0–10	40–75
Sandy clay	..	..	0–10	40–75
Fine sandy clay	..	..	0–10	40–75
Silty loam	..	..	30–56	10–27
Loam	..	..	20–40	20–40
Clay loam	..	..	10–27	30–56
Loamy silt	..	..	40–69	10–33
Silty clay loam	..	..	27–49	27–49
Clayey silt loam	..	..	27–49	27–49
Loamy clay	..	..	10–33	40–69
Silt	..	..	65–100	0–35
Clayey silt	..	..	18–65	18–65
Silty clay	..	..	18–65	18–65
Clay	..	..	0–35	65–100

Gravel—a Fifth Separate

A fifth separate characterizing many soils is gravel, or fine stones and rubble. This is included in the fraction coarse sand and gravel, but in

cases where this coarser material predominates it is required to qualify the soil class. Thus, gravelly clays, gravelly fine sands, or even gravels may frequently be met with, and yet are not specifically classed as such if the material not passing through a 2-mm. round-hole sieve is discarded. Texture may very well be defined as soil quality resulting from the proportional quantities of sands, silt, and clay, but many practical field men are well aware of the influence of gravel and the moderately coarse stony material in arriving at a definition of texture. Naturally, an upper limit must be set to the size of these bodies, and it was suggested earlier in this paper that the limit be set at 1 mm., materials above which may reasonably be assumed not to affect the texture or 'feel' of a soil.

The actual technique employed by the writer is to gently rub the sands on the oven-dried 70 I.M.M. sieves with the finger (dry sieving), and weigh the quantity of fine sand thus obtained. This is added to the amount found later after sedimentation. The material retained by the 70 I.M.M. sieve is first weighed as coarse sand and gravel, then emptied into a 1-mm. round-hole sieve, and again rubbed through with the finger. The material retained is the gravel, and that passing through the coarse sand, each fraction being weighed separately.

For gravel as a fifth separate to qualify the textural class the writer proposes the following: Should the material retained by a 1-mm. round-hole sieve in the coarse sand and gravel fraction lie between 20 and 40 per cent. (the four fractions inclusive of gravel being calculated to 100 per cent.), then the term gravel or rubble is to be prefixed to the textural class, e.g. gravelly loam, gravelly fine sand.

Should the percentage of this material lie between 40 and 65 per cent., then the terms gravel or rubble are to be appended, e.g. sandy gravel, clayey gravel. Lastly, should the percentage exceed 65 per cent., as it may frequently do, the soil is to be termed a gravel or a rubble, as the case may be.

Coarse granite soils in Natal have been found to contain horizons with over 70 per cent. of material retained by the 1-mm. round-hole sieve.

The following examples will serve to illustrate the textural classification of soils containing more than 20 per cent. of gravel:

Coarse sand and gravel %	(*Gravel* %)	*Fine sand* %	*Silt* %	*Clay* %	*Textural class*
43	(41)	28	21	8	Loamy coarse sandy gravel
43	(22)	28	21	8	Gravelly loamy coarse sand
43	(22)	3	8	46	Gravelly coarse sandy clay
43	(41)	3	8	46	Clayey gravel

Concluding Remarks

The diagram presented in this paper was not arrived at solely by a representation of field estimates of texture, since the writer concludes such estimates vary so much among themselves as not to warrant being the starting-point for defining a textural class on the basis of its actually determined composition.

While the ranges of fractions in the textural classes proposed in this paper do not differ very considerably from those formulated in the past, the writer believes that these textural-class names depict more exactly what the soil is. For example, a soil containing 44 per cent. fine sand and 50 per cent. clay is better described as a fine sandy clay than as a medium clay. An attempt to co-ordinate a very large variety of field estimates of texture cannot provide an absolute basis, the writer's own long experience with soils both in the field and in the laboratory having convinced him that many individual workers are quite incapable of arriving at a suitable degree of unanimity in their judgements. The writer, therefore, prefers to regard all field estimates of texture as purely provisional until their composition has been ascertained by mechanical analyses and their textural class established by reference to the diagram he has devised. In soil-survey work he selects certain test pits typical of a soil series and subjects the horizons to mechanical analysis. Whatever estimates of texture he has made in the field are then adjusted, if necessary, to represent the textural class according to the diagram presented in this paper.

Summary

Reference is made to the undesirability of discarding material which does not pass a 2-mm. round-hole sieve, previous to mechanical analyses. It is recommended, also, that there should be a reversion to the former lower limit of 1 mm. for gravel and an adjustment to 10 mm. for the upper limit of this material, which should be reported separately and inclusive of the coarse-sand fraction.

A new diagram is presented for the textural classification of soils and employs all four international fractions in assessing the textural class, gravel also being taken into consideration.

It is claimed that while the submitted diagram is not founded entirely on field estimates of texture, as in the case of the triangular system, it provides a truer and more detailed representation of the textural class, to which field estimates must be adjusted in the laboratory.

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THE EQUILIBRIUM OF RAIN-FED GROUND-WATER RESTING ON DEEPER SALINE WATER: THE GHYBEN–HERZBERG LENS

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PROBLEMS of the flow of liquids under gravity in porous materials involve a consideration of free surfaces, i.e. water-tables and surfaces of seepage. These features, and particularly the former, present formidable impediments to mathematical treatment. Such treatment is essentially a discussion of Laplace's equation, and solutions have been carried through to completion in only a few special cases of particular problems (Gustafsson, 1946; Muskat, 1947; Wedernikov, 1946 and 1949), mainly by transformations of the systems as represented in the hodograph plane. Alternative and more certain procedures are (*a*) the use of hydraulic scale models, and (*b*) by analysis as far as to set up appropriate potential functions and to elucidate boundary conditions, the solution being finally completed by numerical methods or by means of electric analogues. The first method certainly provides a numerical solution to the particular problem, but so little analysis is demanded that there is but little clarification of the fundamental situation. The method of electric analogues has been applied with success to single-liquid problems underlying land drainage (Childs, 1943–7); the present paper extends this application to the two-liquid problem of the equilibrium of the Ghyben–Herzberg lens. This equilibrium has relevance both to drainage problems as in certain Dutch polders (particularly such as have been recently inundated by sea-water) and to problems of water-supply, as, for example, in the Dutch dune area (Krul and Liefrinck, 1946) and in Hawaii (Wentworth, 1947).

The nature of the problem may be explained by reference to Fig. 1. Here we see in cross-section a permeable deposit resting upon an impermeable bed *KL*, as, for example, a sand bank resting upon clay. The whole is submerged beneath the sea save for the top of the permeable layer. If this latter is of considerable extent, then the surface *AB* of the sea on one side is not necessarily at the same level as that, *DE*, on the other, and there will be a flow of salt ground-water from one side to the other. The steady state without rainfall is shown in diagram *a*, where the water-table (the locus of points at zero hydrostatic pressure and approximately the upper boundary of the ground-water) is the streamline *BCG*. Suppose now we have rainfall of intensity *a* cm./sec. superimposed on this picture; the result is shown in diagram *b*. The new water-table *FCG* is higher, providing the pressure-head needed to dispose of the rainfall as drainage; it bounds fresh and not salt ground-water; and it is no longer a streamline. The salt-water boundary is depressed to the position *HJ*, and no longer satisfies the condition of zero hydrostatic pressure. The complete solution of the problem indi-

cated by diagram *b* comprises the delineation of the boundaries of fresh and salt water, together with the flow net (equipotentials and streamlines) within each body of ground-water, for given permeability and geometrical configuration of the permeable deposit, sea-levels, density of sea-water, and rate of rainfall. In the non-steady state the boundary $H\mathfrak{J}$ is no longer a streamline, and the solution for a given instant of time will be a function of past history.

We first set up the two potential functions ϕ and ϕ' relating to the

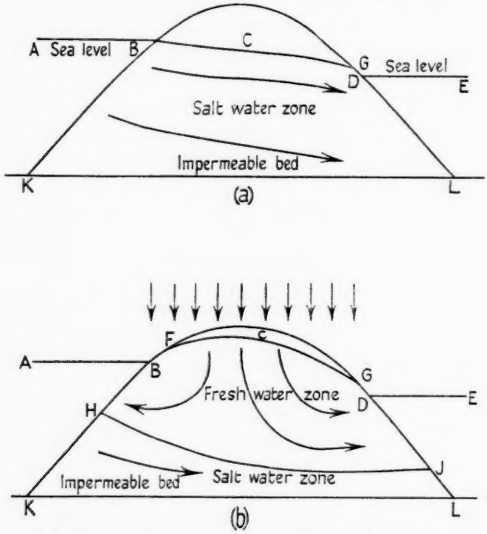

FIG. 1. Illustrating the development of the Ghyben–Herzberg lens. In diagram *a* salt water flows in the partially submerged bank from the side of high sea-level to that of low sea-level. In diagram *b* precipitation causes a 'lens' of fresh ground-water perched upon a depressed salt ground-water zone. The arrows show the general direction of flow of water.

bodies of fresh and salt water respectively, the potential at a point being defined as the work done in taking unit volume of the appropriate liquid to that point from an arbitrarily chosen point at which the potential is defined to be zero. It follows that

$$\left.\begin{aligned}\phi &= p+g\rho h\\ \phi' &= p+g\rho' h,\end{aligned}\right\} \qquad (1)$$

where p is the hydrostatic pressure and h is the height at the point, both relative to the point at zero potential, whilst ρ and ρ' are the densities of fresh and sea water respectively.

We next assume the validity of Darcy's law in each zone, namely that the effective flow velocity, v, is given by

$$v = -K \operatorname{grad}(\phi)$$

or

$$v = -K' \operatorname{grad}(\phi'),$$

where K or K' is the permeability of the material to the liquid in question. The range of validity of this law has been adequately discussed by Muskat; it is enough to say here that in drainage problems the Reynolds number does not exceed the critical value above which the law is invalid except in quite extraordinary circumstances, as, for example, when there is a potential gradient as great as g in a saturated coarse sand of as much as 2 mm. grain size. Deriving the equation of continuity in the usual way from the flow law leads to Laplace's equation

$$\nabla^2(\phi \text{ or } \phi') = 0. \tag{2}$$

We must now elucidate the boundary conditions. For the water-table FCG we have

$$p = 0, \qquad \phi = g\rho h. \tag{3}$$

For the surfaces of seepage BF and DG condition (3) also holds: the difference between these surfaces and the water-table is that the positions of the former (but not, of course, their extent) are initially defined whilst the flux remains to be found, whilst at the latter the flux is initially defined and the position remains to be found. At the surfaces BH and $D\mathcal{J}$, where fresh ground-water seeps out to mix with sea-water, we have hydrostatic pressures which are readily calculable, since pressure is continuous across the boundary and therefore equal to the pressure of the head of sea-water at the point considered. We assume that the rate of mixing of the emergent water with the sea is such that the density of the sea-water at the boundary is the normal value ρ'. If we take the point D to be our arbitrary potential datum (i.e. of height and of pressure), then the value of h for a point on $D\mathcal{J}$ at depth d below the surface is $-d$, and the pressure is therefore $-g\rho' h$. Similarly, a point on BH at depth d' below the surface B has a height h of $-(d'-\delta)$, whence the pressure, $g\rho' d'$, is given by $-g\rho'(h-\delta)$, where δ is the height of B above datum.

Substituting these values of p in (1), we have, along $D\mathcal{J}$,

$$\phi = -gh(\rho'-\rho) \tag{4}$$

and along BH

$$\phi = -gh(\rho'-\rho)+g\rho'\delta. \tag{5}$$

Along $\mathcal{J}L$ we have salt water flowing in the material and consequently the appropriate function is ϕ'. Substituting the above values of p in (1) we have

$$\phi' = 0, \tag{6}$$

whilst along HK

$$\phi' = g\rho'\delta. \tag{7}$$

The impermeable bed KL is an initially specified streamline, whilst the interface $H\mathcal{J}$ is defined by the condition that pressure is continuous across it, i.e.

$$\phi'-\phi = gh(\rho'-\rho). \tag{8}$$

In the steady state $H\mathcal{J}$ must clearly be a streamline, since a flux across it implies a moving boundary. In general, however, fluctuations of rainfall will result in both a moving water-table and a moving boundary between salt and fresh water. These movements introduce components of flux proportional to the rate of rise or fall of the boundaries considered. Owing to the sensibly incompressible nature of water, solutions of the non-steady state may be regarded as those of a sequence of steady states

with the boundary conditions specified above. Solutions of the non-steady state in this way have been already demonstrated in a single-liquid drainage problem (Childs, 1947).

The possibility of constructing an electric analogue of this hydraulic problem rests on the formal identity between Darcy's and Ohm's Laws, leading to formally identical equations of continuity (namely Laplace's equation) in aquifers and electric conductors. The equivalence between the boundary conditions of the hydraulic prototype and of the electric analogue has been discussed in some detail for drainage problems (Childs, 1945*b*), including the non-steady state (Childs, 1947). For the present problem the equivalence is indicated in Table 1, in which V is the electric potential at a point on the analogue, simulating the potential ϕ at the corresponding point on the hydraulic prototype. The analogue being an electric conductor of relatively low conductivity, shaped to represent the water-conducting body to scale, conditions (2) to (6) of Table 1, column 3, are imposed upon it by the laboratory manipulation of sealing on electrodes of relatively low resistance maintained at the appropriate electric potentials, the sealing material being colloidal graphite paste ('Aquadag'). It is usually convenient to define the particular state of water-table to be studied by fixing initially one point on the water-table, say the mid-point, then to adjust the currents representing known boundary fluxes to convenient values (the electric potential value at that point thereby being fixed in the analogue), and to adopt the value of α which emerges. The fresh and salt water bodies are conveniently represented by separate analogues, the upper boundary of the latter always necessarily having the same shape as the lower boundary of the former. The element of trial and error enters into the construction of the analogue in the finding of surfaces satisfying at the same time conditions (1) and (7) for the water-table and interface respectively, whilst the electric current distributions (led in by distributed electrodes) truly reflect to scale the water fluxes of the prototype. It has been shown that the upper unsaturated soil above the zone of ground-water may be ignored, serving only to conduct precipitated water in sensibly vertical streamlines to the ground-water zone (Childs, 1945*b*). This latter is, strictly, bounded at the top by the capillary fringe boundary and not by the water-table. However, the capillary fringe is not likely to be of appreciable thickness to the scale of such problems as the present, but cases of field drainage, where it may be important, have been discussed (Childs, 1945*a*). It will be ignored here.

The cases presented here are all highly idealized, since there is no object in undertaking the arduous labours associated with hypothetical cases of a realistic kind; only real cases where a practical solution is required would warrant the work. The method is equally well demonstrated with simplified boundary conditions. In the first place we assume uniformity in a direction perpendicular to the cross-section, a condition which would be approximately satisfied in a long narrow bank. The problem then becomes two-dimensional and we can employ, as our analogue, the very convenient sheet conductor provided by paper sprayed with 'Aquadag' colloidal graphite, which is readily cut to any

shape desired. Secondly, we take as our permeable body a vertical-sided 'dyke' based on a flat horizontal bed. Steady states only are dealt with here, since the non-steady state has been demonstrated in another connexion (Childs 1947) and its consideration would contribute but little to the present discussion.

The analogue having been successfully prepared, the potential field is then systematically explored within its boundaries and equipotentials

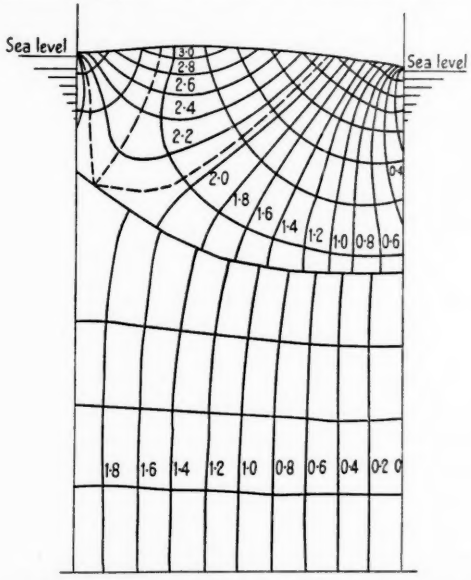

FIG. 2. Solution of a particular case, highly idealized. Interpretation to a desired scale is explained in the text. If the width of the 'dyke' is 100 metres, it is submerged to a depth of 155 metres on the left and to 150 metres on the right, whilst the water-table peak is 8 metres above the lower sea-level. The equipotentials are marked in arbitrary units, with intervals of 0·2 unit.

drawn at convenient intervals of potential. The streamlines are then drawn in freehand in the usual way to provide an orthogonal family of curves constituting the flow net. The equal intervals between streamlines may be ensured since these streamlines intersect the water-table, at which the current distribution is known.

The first example presented, shown in Fig. 2, is of a case of differing sea-level on the two sides of the 'dyke', for a particular height of water-table at the mid-point determined by a particular relationship between rainfall rate and permeability. The value of ρ'/ρ adopted is the reasonable one of 1·02. The remaining cases, illustrated by Figs. 3 to 5, are for a similar dyke but with the same sea-level on both sides, and for five different rainfall rates. Fig. 3 shows, on one diagram, the successive water-table stages 1 to 5 and the successive interface stages 2′ to 5′. At stage 1 the rainfall rate is sufficient to exclude salt water from the body

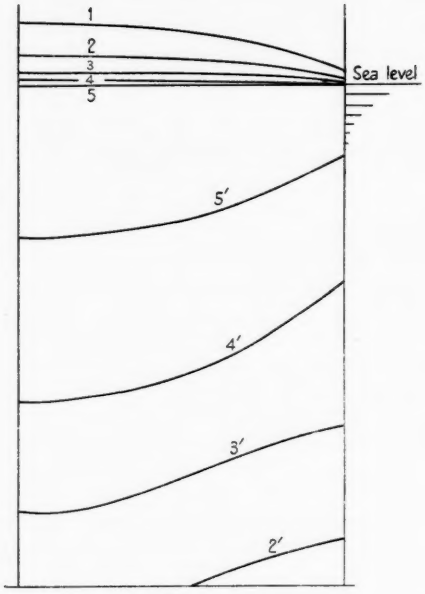

FIG. 3.

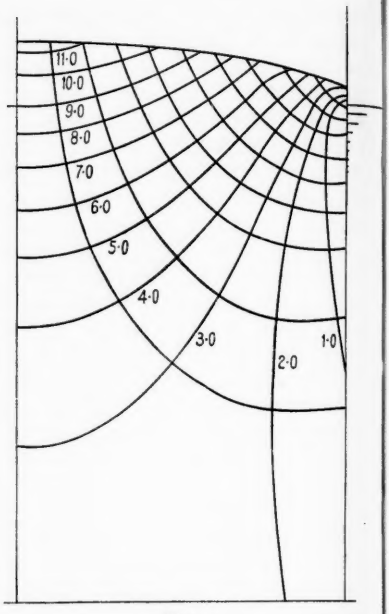

FIG. 4.

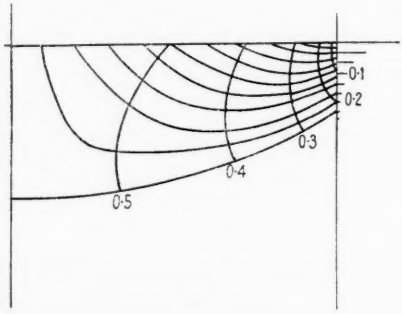

FIG. 5.

FIG. 3. Boundaries in a set of solutions for a dyke with the sea at the same level on each side. Only one-half of the dyke thickness is shown, since the flow net is symmetrical about the medial plane. Curves 1 to 5 show the water-table and 2′ to 5′ the boundary between salt and fresh ground-water for rainfall rates descending in the ratios 1·0 : 0·52 : 0·22 : 0·09 : 0·02 respectively. At the maximum rate salt water is excluded from the dyke.

FIG. 4. The flow net for boundary 1 of Fig. 3. The potentials are indicated in arbitrary units.

FIG. 5. The flow net for boundary 5–5′ of Fig. 3. The potential units are the same as in Fig. 4.

of the dyke. Figs. 4 and 5 show the flow nets for the two extreme stages. Since each of these cases is symmetrical about a medial vertical plane perpendicular to the cross-section, only one-half of each flow net is shown and only one-half was represented in the analogue. The other half is just the mirror image of that shown. The rainfall rates, as indicated by the current input at the 'water-table', the value of α being the same for all the figures, are proportional to 1·00, 0·52, 0·22, 0·09, and 0·02, respectively. It is clear from Table 1 that the construction of these

TABLE 1

	Surface	*Potential at surface*	*Corresponding analogue potential*	*Relation between constants of column 4*
1.	Water-table *FCG*	$\phi = g\rho h$	$V = \alpha h$	α arbitrary
2.	Surfaces of seepage, *DG* and *BF*	$\phi = g\rho h$	$V = \alpha h$	
3.	*DJ*	$\phi = -gh(\rho'-\rho)$	$V = -\beta h$	$\beta/\alpha = (\rho'-\rho)/\rho$
4.	*BH*	$\phi = -gh(\rho'-\rho)+g\rho'\delta$	$V = -\beta h+\alpha'\delta$	$\alpha'/\alpha = \rho'/\rho \doteqdot 1$
5.	*JL*	$\phi' = 0$	$V' = 0$	
6.	*HK*	$\phi' = g\rho'\delta$	$V' = \alpha'\delta$	
7.	*HJ*	$\phi'-\phi = gh(\rho'-\rho)$	$V'-V = \beta h$	

analogues is a good deal simpler than that of Fig. 2. Since δ is zero, condition (6) repeats (5), i.e. ϕ' is zero throughout the salt-water zone and the salt water is stagnant. Condition (7) is then independent of any consideration of the salt-water zone and becomes

$$\phi = -gh(\rho'-\rho)$$
$$V = \beta h,$$

and one analogue only, that of the fresh-water zone, needs to be constructed.

Interpretation of these flow nets to any desired scale is a simple matter. Let us, for example, consider Fig. 2, and let us suppose that the 'dyke' represented has a width of 100 metres. All the boundaries are then to the same scale. The indicated electric potentials are all arbitrary, being in fact merely potentiometer readings unconverted to any particular practical unit. They may be converted to ergs in the prototype by consideration of any point on the water-table (a surface of seepage would also serve). For any point on the water-table

$$\phi = g\rho h;$$

hence at the highest point, at a height of 800 cm. ρ being unity

$$\phi = 800g \text{ ergs.}$$

The electric potential indicated here (see Fig. 2) is 3·1 arbitrary units hence

$$1 \text{ arbitrary unit} = 800g/3{\cdot}1 = 25{\cdot}3 \times 10^4 \text{ ergs.}$$

Now consider an element of the flow net bounded by two neighbouring equipotentials and two neighbouring streamlines of Fig. 2, situated in

the fresh-water zone, and 1 cm. in thickness perpendicular to the cross-section. If the width between streamlines at the element chosen is W and the length between equipotentials is L, we have a flow element of cross-section $W \times I$ and length L accommodating a flow of Q with a potential difference $\Delta\phi$. Applying Darcy's law to the element

$$Q = KW\Delta\phi/L. \qquad (9)$$

$\Delta\phi$ is known, since it is represented by 0·2 arbitrary electric units in the analogue, as may be seen in Fig. 2.

$$\Delta\phi = (0{\cdot}2)(25{\cdot}3 \times 10^4) \text{ ergs.}$$

W/L is independent of scale and may be found by measuring in the diagram as many 'rectangles' of approximately equal area as possible and taking the mean. It is a consequence of uniformity of permeability that W/L should be the same for all the 'rectangles' of the flow net. In our case

$$W/L = 2{\cdot}25.$$

Q is known since each stream tube cuts the water-table over an area of 10 m.* × 1 cm., receiving precipitation at a rate of a cms./sec.

$$Q = 1000a \text{ cc./sec.}$$

Substituting these values in (9), we get

$$1000a = 11{\cdot}4 \times 10^4 K,$$

or

$$a/K = 114 \text{ c.g.s. units.}$$

This particular stream picture is therefore true for the boundary conditions quoted and for all values of rainfall and permeability which have the ratio $a/K = 114$ c.g.s. units. To take matters a step farther, if, for example, the material is a fine sand with a permeability of, say, 10^{-7} c.g.s. units, the appropriate rainfall resulting in the given flow net is

$$a = 114 \times 10^{-7} \text{ cm./sec.,}$$

or approximately 1 cm. per day.

It will be noticed that the permeability K does not enter into the solution until we require to calculate rates of flow in the material. The rate of flow of fresh water, being given by the rainfall, dominates the picture and must be calculated. The rate of flow of sea-water in the lower zone is consequential; the dominating sea factor is the difference of level δ, which is initially known. We are not much interested in the flow of sea-water, but if required for completeness we may draw in the streamlines, as has been done in Fig. 2 below the interface, on the assumption that the permeability to sea-water differs only negligibly from that to fresh water, W/L being made the same as for the fresh-water zone. The total number of streamlines then gives the total flow. This procedure obviates the measurement of current distribution at controlled potential boundaries, which presents unwarranted complications.

Summary

When precipated fresh water falls on land already occupied by sea-fed salt ground-water, we have a dynamic equilibrium with fresh ground-

* The ten 'stream tubes' divide the total width of water-table, 100 m., equally, since rainfall is uniform.

water perched upon the salt ground-water. The configuration is known as the Ghyben–Herzberg lens. In this paper potential functions are set up for the separate ground-water bodies and the boundary conditions are elucidated. By means of electric analogues certain particular and idealized cases are completely solved, all being steady states, although the procedure for non-steady states is indicated. The cases solved are for different sea-levels on the two opposite sides of an idealized dyke, and for the same sea level on the two sides but for five different rates of rainfall, in each case the configuration of all boundaries and also the flow nets being presented.

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THE INFLUENCE OF HUMUS ON SOIL AGGREGATION

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WITH PLATES I TO IV

Summary

SEVERAL methods were used for extracting humus from a number of widely different soil types. The cementing power of the various humates was tested by mixing them with soil and determining the weight of water-stable aggregates surviving wet sieving. In general, α-humic acid > Tiulin's group-2*b* humates > group-2*a* humates > group-1 humates > fulvic acid. Greater stability was obtained when the humates were fixed as films over the soil particles by H or Ca ions.

An attempt was made to fractionate humic acid into its component colloidal cements without success. Various chemical treatments, such as hydrolysis, deamination, esterification, and acetylation modified the glueing qualities of humic acid, suggesting that colloidal substances with NH_2, COOH, and OH polar groups were partly responsible for the cementing action of humates.

A study was made of the influence of various organic substances on soil aggregation. Resins, fats, and some proteins cemented soil into aggregates so impervious to water that slaking was prevented. Some microbial gums and other polysaccharides acted as good soil glues, while others were useless. Lignates were only slightly inferior to humates as soil cements, but tannin and cationic detergents were of little value. The glueing properties of proteins and polyuronides were considerably altered by various chemical treatments.

The structure of puddled soils was sometimes restored by repeatedly wetting, incubating, and drying them. Acid, lateritic soils high in sesquioxide cements were rapidly restored; chernozems containing much colloidal humus and clay took longer, but other types showed little improvement even after prolonged treatment. Sterilization of soil rendered the humus more available for micro-organisms, which were then able to improve soil structure temporarily. Micro-organisms reduced the stability of aggregates cemented by films of calcium humate.

This paper examines the possibility of colloidal humus constituents acting as soil cements. Geltser (1936, 1937, 1943) claims that only readily decomposable organic materials improve the physical condition of soil. She considers that resistant humus is practically inert and plays little part in cementing soil particles into water-stable aggregates. Many soils, however, such as lateritic red loam, chernozem, rendzina, and terra rossa possess good crumb structure even after the nutritive humus is exhausted through long periods of continuous cultivation. It is doubtful whether they owe much of their permanent structure to fungal hyphae and capsulated bacteria. McHenry (1945) also considers that too much attention has been given to the frail crumbs formed by micro-organisms and not enough to the strong aggregates present in many soils.

Demolon and Hénin (1932) studied the relative aggregating powers of humus and clay. Sideri (1930, 1938*a*, 1938*b*) postulated that soluble humates were orientated by clay particles, thus forming films. On drying, these films became irreversible so that they cemented aggregates together even when re-wetted. Myers (1937) showed that humates acted as better cements in the presence of Ca and H ions than Na ions. He considered that the humates were bound to negatively charged clay micelles through polar groups, such as COOH.

Tiulin (1938*a*, 1938*b*, 1946) classified soil organic matter into loosely bound humates of Ca and Mg and those firmly bound by Fe, Al, or clay. These could be separated by fractional peptization using different concentrations of sodium hydroxide. He found that chernozems with good structure contained relatively high amounts of the former, while podzols with poor structure contained large quantities of the latter combinations. Jung (1943) and Meyer (1941) considered that part of the humus was adsorbed to clay by polar bonds and part by molecular and van-der-Waals forces. Chapek and Sakun (1944) thought that most of the humate was held mechanically and only a small fraction was adsorbed onto clay. McHenry (1945) and Peterson (1946) studied the influence of clay minerals on the stability of organo-mineral aggregates and concluded that clays with a high cation-exchange capacity gave better aggregation than those with a low exchange value. Electron-microscope studies of natural soil aggregates by Kroth and Page (1946) showed that clay particles were covered with humus, and they concluded that humus was adsorbed to the clay and was not merely entangled.

Practically nothing is known concerning the cementing power of the various constituents in humus. Fuller (1946, 1947*a*, 1947*b*) has obtained evidence that uronides occur in humus, while Forsyth (1947) has isolated a small amount of polyuronide from fulvic acid. Martin (1945, 1946), McCalla (1946), and Geoghegan and Brian (1946) have found that bacterial and other polysaccharides aggregate soils. Kojima (1947*a*, 1947*b*) detected appreciable quantities of amino acids in peat, thus suggesting the presence of proteins, and McCalla (1946), Kroth and Page (1946) have observed the glueing power of undecomposed proteins. Waksman (1938) and Gillam (1940) gained evidence that lignin-like substances were present in humus, and McCalla (1945), and Alderfer, Gribbins, and Haley (1944) have shown that such substances are capable of aggregating soils.

Experimental Methods

Extraction of humates from soils

Several methods were used for extracting humates from soils. Waksman's method (1938) of removing humus with cold 2·5 per cent. NaOH and precipitating α-humic acid with HCl yielded more cementing substances than either extraction with boiling NaOH or with cold, neutral Na pyrophosphate or Na citrate. Fulvic acid and β-humus were dialysed against HCl to remove large quantities of iron and aluminium invariably present. Tiulin's group 1, 2*a*, and 2*b* humates were prepared

according to the technique adopted by Atkinson and Turner (1944) using distilled water, 0·004 N. NaOH, and 0·01 N. NaOH respectively for extracting the Na-saturated soils. To prevent rapid autoxidation and microbial spoilage suspensions of all the above humate fractions were preserved at pH 6·5 under toluol, and before use they were adjusted to pH 8·5 with NaOH. The amount of humate in solution was determined by drying an aliquot and finding the loss of weight on ignition. The percentage of organic matter in soils was determined by the wet-oxidation method of Walkley and Black (1934) except in the case of peats when loss on ignition was used.

Production of microbial gums

Bacteria and fungi were cultivated for 20 days at 25° in shallow layers of liquid medium containing 2·0 per cent. of glucose, 0·5 per cent. of peptone, and the usual salts. The bacterial cells were removed by centrifuging while the fungal hyphae were collected on a Buchner filter.

Bacterial gums were prepared from the metabolic solution by precipitating them with 3 volumes of ethanol, filtering off the floc, washing it with ethanol, dispersing in water, dialysing to remove salts, repeatedly shaking with chloroform to remove proteins, re-precipitating with 3 volumes of ethanol, filtering off, washing with ethanol, and drying at room temperature.

The fungal hyphae were composted for 20 days at 25° after inoculating with soil suspension, and a gum was isolated from the sludge by the technique used for preparing bacterial polysaccharides.

Production of soil aggregates

Usually triplicate 25-gm. or 50-gm. portions of Rothamsted allotment soil (< 1 mm.) were thoroughly mixed with humates or other cementing substances dissolved in sufficient volume of water to bring the soil to sticky point. The aggregates were conditioned overnight to allow the solutions to form films around the soil particles, then dried at 50°. In some cases the films were immobilized or fixed by spraying the dry crumbs with either dilute HCl or $CaCl_2$, allowing the solutions to penetrate over a period of several hours, then redrying the crumbs at 50° C.

Aggregate analysis of soils

Macro-aggregates > 1 mm. in diameter were determined by soaking 25 gm. or 50 gm. of soil crumbs in water for 24 hours, transferring the wet soil to a sieve with 1-mm. holes, and hand-sieving under water until all fine particles had passed through. This usually required 20 strokes. The water-stable aggregates retained on the sieve were dried at 50° and weighed.

Experimental Results and Discussion

Aggregating power of various humate fractions

1. *Extraction of fractions from various soils.* Humates were extracted from 10 soils, representing typical krasnozem, chernozem, brown forest, peat, serozem, and weakly podzolized soils using techniques previously

outlined. In general the percentages of humus in the extracts were considerably less than the total amounts in the soil, indicating that part of the humus was very firmly held in the soil. Despite the fact that all of the humus could not be recovered, tests were carried out to determine the cementing powers of some of the different fractions.

2. *Test of humate fractions.* Sufficient volume of Na humate (pH 8·5) was added to 25 gm. of Rothamsted sifted allotment soil (< 1 mm.) to provide 1 per cent. of additional humus. Crumbs were formed by mixing, conditioning overnight, and then drying at 50°. The weight of stable macro-aggregates thus formed are presented in Table 1.

TABLE 1

Influence of Various Fractions of Humus on the Aggregation of Rothamsted Soil

Soil from which humate was obtained	*Mean weight of aggregates > 1 mm./25 gm. soil treated with various humus fractions*				
	Group 1 1st fraction	*Group 2a 1st fraction*	*Group 2b*	*α-Humus*	*Fulvic acid*
Wollongbar	..	0·23±0·05	3·03±0·76	9·54±0·89	..
Moscow	..	2·23±0·24	3·58±0·30	12·10±0·45	..
Glen Innes	..	4·35±0·37	1·82±0·08	11·58±0·63	..
Rothamsted	0·11±0·03	2·88±0·25	1·13±0·03	10·81±0·76	..
Hertford (peat) (0″–4″)	0·26±0·07	0·55±0·20	2·75±0·29	15·71±1·03	0·18±0·04
Hertford (peat) (2 ft.)	5·59±0·66	4·93±0·42	3·90±0·51	..	1·20±0·08
Ely (fen)	..	..	..	10·44±0·39 (NaOH) 6·06±0·23 (Na pyrophosphate) 4·36±0·12 (Na citrate)	1·17±0·35
Narellan	0·20±0·07	2·64±0·52	4·42±0·49	6·23±0·35	0·54±0·19
Control	0·13±0·03				

In two instances out of four, the first fraction of group-1 humus was a poorer cement than that from group-2*a* humate, and in three cases out of seven, group 2*a* was inferior to group 2*b*. Fulvic acid was a consistently poor glueing material. In all cases α-humus was greatly superior to any other humate fraction, and for Ely fen NaOH extract was better than Na pyrophosphate or Na citrate. Plate I *a* shows the relative amounts of stable aggregates formed by different humus extracts from Narellan soil.

These results suggested that greater amounts of the real organic cements from soils were removed with the higher concentrations of NaOH.

During wet-sieving operations it was observed that much of the brown Na humate added to the soil diffused into the water, and experiments were conducted to determine whether greater aggregation would be obtained if the humus films were immobilized by treatment with HCl or $CaCl_2$.

3. *Fixation of humates with* HCl *and* $CaCl_2$. As previously, 1·0 per

cent. of Na α-humate from 8 soils was mixed into 25-gm. samples of Rothamsted soil, and after drying, three sets were treated by spraying with 10 ml. of H_2O, 0·1 N. HCl or 0·1 N. $CaCl_2$, respectively. The humates from the various soils differed slightly in their cementing powers, but in the majority of cases $CaCl_2$ and HCl both slightly improved the structure caused by α-humate. This seemed to be due to the greater fixation of α-humate inside the soil aggregates rather than to any influence of the electrolytes on the clay, since the control was not altered significantly with HCl and $CaCl_2$. Plate I*b* shows the relative influence of Na^+, H^+, Ca^{++}, and Fe^{+++} ions in cementing Glen Innes α-humate to Rothamsted soil.

Under the microscope the humus seemed to be present either as films around macro-aggregates of clay or as particles of precipitated humate.

Incidentally it was found that freshly precipitated, washed, H, Ca, or Fe humate when mixed with soil possessed very little cementing power, showing that the humate films had to spread over the soil particles before being fixed with electrolytes. The addition of 0·25 gm. of H, Ca, and Fe humate to 24 gm. of Rothamsted soil (< 1 mm.) gave 0·47 gm., 0·39 gm., and 0·72 gm. of aggregates > 1 mm. diameter respectively. These values were not significantly different from the untreated soil which contained 0·21 gm. of aggregates. Even after a long period of incubation with micro-organisms the humus precipitates improved in cementing quality only slightly, yielding 2·07 gm., 3·41 gm., and 1·84 gm. of aggregates respectively. The addition of NaOH overnight followed by HCl produced a great improvement, giving 9·48 gm., 7·94 gm., and 7·26 gm. of aggregates respectively. It is known that humates contain proteins, polyuronides, and phenolic substances derived from lignin and it is possible that polar bonding takes place between the NH_2, COOH, phenolic and alcoholic OH groups present in the humus and the negatively charged clay.

Attempts were made to determine the polar groups and the types of substances responsible for the cementing properties of soil humates. This was done by subjecting humates to various chemical treatments.

4. *Influence of chemical treatments on aggregating power of α-humus.* Sodium α-humate from Grafton soil was used throughout this experiment. Tests were made to determine the cementing power before and after boiling the humate under neutral, acid, and alkaline conditions and after extraction with ether and cold hydrochloric and acetic acids. The glueing properties of deaminated, esterified, and acetylated humates were also determined. Free NH_2 groups were destroyed by deamination at room temperature with nitrous acid. The COOH and OH groups were modified by esterification with methanol and acetylation with acetic anhydride by the methods used by Forsyth (1947*a*). A test was made after oxidizing the humate with alkaline hypoiodite using the method of Norman (1943). The cementing power of humate mixed with formalin was also determined. Sufficient amounts of these chemically treated humates, dispersed in NaOH (pH 8·5), were mixed with 25 gm. of Rothamsted allotment soil (< 1 mm.) to provide 1·0 per cent. The

aggregates were subsequently treated with $CaCl_2$, then wet-sieved as usual. The results are presented in Table 2.

TABLE 2

Influence of Chemical Treatments on the Aggregating Power of α-Humus

Chemical treatment	*Mean weight of aggregates > 1 mm./25 g. soil*
Untreated humate	14·94±0·82
Boiling (pH 7)	16·81±0·78
Acid hydrolysis (0·1 N. HCl, 1 hour)	6·25±0·22
(N. HCl, 1 hour)	1·83±0·18
Alkaline hydrolysis (N. NaOH, 1 hour)	2·31±0·32
Cold 2 N. HCl wash	14·63±0·94
Cold 2 N. HAc wash	9·35±0·73
Ether extracted	14·52±1·05
Deamination	6·78±0·98
Esterification	13·20±0·18
Acetylation	9·75±0·73
Oxidation (hypoiodite)	3·43±0·35
Formalin	17·13±0·52
Control (no humate)	0·21±0·35

Evidently the cementing substances in α-humus are not affected adversely by boiling at neutrality, but acid or alkaline hydrolysis destroys them. This suggests that colloidal proteins or polysaccharides might be important. Leaching the α-humic acid with hydrochloric acid does not remove any cementing material, but acetic acid removes something which is valuable. Ether extraction has no effect, indicating that resins, fats, and waxes are probably not responsible for the binding power of humates. Deamination considerably reduced aggregation, thus suggesting that either proteins or aminopolysaccharides are affected. Esterification only slightly decreases the cementing power, thereby indicating that the carboxyl groups of proteins and polyuronides are of only small importance in polar bonding. Acetylation lowers the aggregating properties of α-humus, and this implies that phenolic and alcoholic OH groups (and possibly NH_2 groups?) are important. Oxidation with alkaline hypoiodite is supposed not to affect polysaccharides, but to destroy lignin-like materials. This treatment considerably reduced cementation by α-humate, so that lignin derivatives might play a part in aggregate formation. Formalin caused a rise in the number of water-stable crumbs, thus indicating that plastic-like polymers may have been formed with phenolic products from the oxidation of lignin or with proteins. Some of these points are illustrated in Plate II*a*.

These experiments provide indirect evidence that amino-polyuronides, proteins, polysaccharides, and lignin-like colloidal materials might all contribute to the cementing action of soil humus.

Aggregating power of various organic substances

1. *Influence of various substances on aggregation.* All attempts at isolating proteins and polyuronides from humic acid failed, so accessible

substances were used to determine their influence on cementation of soil. In addition lignates, tannins, and fats were tested. In view of recent work on stabilization of earth roads with resins, cationic detergents, and cement, some of these substances were also included.

Representatives of each of these materials were mixed with 50 gm. of Rothamsted allotment soil (< 2 mm.) to provide 0·5 per cent. concentration, dried, then wet-sieved as usual. Space does not permit tabulation of the results which, however, may be summarized as follows.

Two resins were used, and Vinsol gave better aggregation than sodium rosinate, but the soil was very difficult to wet after treatment. Fats produced very stable crumbs which were almost waterproof. Sodium stearate neither aggregated soil nor impeded wetting, probably because most of the soap diffused into the water during soaking.

The polysaccharides varied greatly in their ability to cement soil. Gum from Geoghegan's strain of *B. subtilis* gave excellent aggregation, that from *Bacillus polymyxa* produced fairly good aggregation, while polyuronides from *Achromobacter spp.* were only fair to poor cements. The best bacterial cement did not inhibit wetting of the soil, but three other gums considerably reduced the wettability. Polysaccharide isolated from decomposing fungal hyphae of *Aspergillus nidulans* possessed good cementing power, but gum isolated from soil fulvic acid was almost useless. It is possible, however, that the soil gum may have been degraded during extractions. Agar proved to be a very good crumb stabilizer provided it was mixed into the soil while hot. It did not inhibit the uptake of water. Pectin, sodium alginate, and gum arabic were poor cements.

The proteins, egg albumen, haemoglobin, and Na caseinate, gave excellent aggregation after a short soaking period, but they acted only as fair cements after 24 hours' treatment. Three other protein-like materials gave practically no stable crumbs and did not impede wetting.

Amongst the lignin-containing substances, Na α-humate and Na lignosulphonate gave moderate aggregation, but the insoluble H and Ca salts of these materials when added to soil were useless.

Sodium tannate did not aggregate the soil.

The cationic detergents were poor crumb stabilizers. One per cent. Portland cement was unable to bind soil particles into crumbs, but 6 per cent. gave fairly good results, although it rendered the soil too alkaline for plants.

It is fairly obvious that two mechanisms are involved in stabilizing crumbs. Substances like fats and resins arrest slaking by rendering the crumbs waterproof. Substances such as *B. subtilis* gum and agar do not affect the wettability of the soil, yet they glue the particles together very efficiently. Other materials depend on both actions, e.g. some proteins, certain bacterial gums, humates, and lignates.

2. *Effect of other chemical treatments.* The free NH_2 groups of two proteins, egg albumen and casein, were destroyed by deamination at room temperature with nitrous acid. The same two dry proteins and also two dry polyuronides, pectic and alginic acids, were esterified with methanol and acetylated with acetic anhydride by Forsyth's methods

(1947*a*) to modify their COOH and OH groups respectively. After chemical treatment the substances were filtered off, washed with 75 per cent. alcohol, and dispersed in NaOH (pH 8·0). It was observed that deaminated and esterified proteins were soluble in NaOH, but the viscosity of the latter solutions was fairly low. Acetylated proteins were only partially soluble in sodium hydroxide. Both esterified and acetylated polyuronides were soluble in NaOH. Sufficient volume of each solution was mixed with 25 gm. of Rothamsted allotment soil (< 1 mm.) to provide 1·0 per cent. of organic colloid. Untreated proteins and polyuronides were added as controls, and as an additional treatment formalin was mixed with the organic colloids. Table 3 gives the results of macro-aggregate analysis.

TABLE 3

Influence on Aggregation of Modifying the Polar Groups on Protein and Polyuronide Cements (Rothamsted Soil)

Substance	*Mean weight of aggregates > 1 mm./25 gm. soil after modifying the cements*				
	Untreated	*Deamination*	*Esterification*	*Acetylation*	*Formalin*
Albumen . . .	24·27	12·70	1·89	0·13	23·84
Casein . . .	24·30	13·69	1·00	3·52	24·61
Pectic acid . .	3·19	..	3·16	0·74	2·27
Alginic acid . .	9·02	..	4·50	8·45	..
Untreated soil control .	0·46				

In the case of chemically unaltered organic cements it was found that both proteins gave excellent aggregation, alginic acid yielded fair, and pectic acid produced poor cementation.

Deamination of the proteins reduced their cementing power, esterification and acetylation greatly decreased the numbers of stable aggregates. It was thought that formalin treatment might form insoluble plastics with the proteins, thus leading to greater binding. But there was no improved cementing action, possibly because aggregation was excellent with proteins alone.

Esterification resulted in loss of cementing power of alginic acid while that of the poor cement, pectic acid, remained unchanged. Acetylation had no appreciable effect on the cementing power of alginic acid, but it greatly reduced the amount of aggregation formed by pectic acid.

Caution should be exercised in interpreting these results. Besides showing the effect of modifying polar groups on aggregation, it is possible that they show also the effect of partially degrading the protein and polyuronide molecules, although only fairly mild chemical methods were used. It seems likely, however, that NH_2, COOH, and OH groups might all be involved in polar linkages between organic and inorganic colloids.

Action of micro-organisms on soil humus

1. *Influence of repeatedly wetting, incubating, and drying aggregates prepared from puddled soils.* McGeorge (1937) and Peterson (1943,

1946) improved the structure of puddled soils by alternately wetting and drying them. They thought that this treatment orientated both clay and humus particles so that these cemented the soil into stable aggregates. An experiment was carried out to find whether this treatment together with incubation with soil micro-organisms improved structure. Twelve clay loam or clay soils, including ten from Australia, one from England, and one from the U.S.S.R., representing typical lateritic red loam, chernozem, brown forest, red-brown earth, serozem, mallee, and weakly podzolized soils were used in this experiment. They were puddled by boiling with water, and half of each sample was treated with successive amounts of boiling hydrogen peroxide (30-volume strength) to oxidize the humus. The slurries from these two treatments were dried, remoistened to sticky point, crumbed, re-dried at 50°, and 50-gm. samples were removed for macro-aggregate analysis. No hydrogen peroxide was detected after drying and the pH of the soil hardly altered as the result of peroxide treatment. The aggregates thus formed were sprayed with water containing minerals and soil inoculum, recrumbed by mixing, and allowed to incubate for 1 week before being slowly dried at room temperature. This process of inoculating, incubating, and drying was repeated 10 times over a period of 14 weeks, then macro-aggregate analysis was done again.

After one wetting and drying only two soils showed appreciable reaggregation and both of these were lateritic red loams containing large amounts of sesquioxides.

These Reddestone and Wollongbar soils yielded $30{\cdot}25 \pm 1{\cdot}83$ gm. and $19{\cdot}27 \pm 1{\cdot}04$ gm. of macro-aggregates, respectively, after being puddled in water, and $22{\cdot}95 \pm 0{\cdot}98$ gm. and $7{\cdot}20 \pm 0{\cdot}47$ gm., respectively, after removal of the humus with peroxide. Next came a weakly podzolized soil which gave $4{\cdot}65 \pm 0{\cdot}42$ gm. of aggregates after water treatment and $4{\cdot}00 \pm 0{\cdot}26$ gm. after peroxide treatment. After these followed an Australian chernozem ($2{\cdot}64 \pm 0{\cdot}30$ gm., water treated; $1{\cdot}42 \pm 0{\cdot}09$ gm., peroxide treated) and red-brown earth ($2{\cdot}35 \pm 0{\cdot}15$ gm., water treated; $1{\cdot}45 \pm 0{\cdot}12$ gm., peroxide treated). Removal of the humus with hydrogen peroxide reduced the reaggregation of these soils. The other soil types remained almost completely disaggregated.

After repeatedly inoculating, incubating, and drying the soils 10 times, the structure of the two laterites was still much better than that of the other soils. The further treatment improved aggregation of Wollongbar soil ($27{\cdot}80 \pm 1{\cdot}07$ gm., water treated; $35{\cdot}07 \pm 0{\cdot}92$ gm., peroxide treated), but not of the Reddestone soil ($31{\cdot}50 \pm 0{\cdot}78$ gm., water treated; $25{\cdot}77 \pm 0{\cdot}64$ gm., peroxide treated). The chernozem, containing 5·42 per cent. humus, also benefited ($11{\cdot}00 \pm 0{\cdot}96$ gm.). The structure of the remaining soils was not restored either in the presence or absence of organic matter.

Evidently the structure of laterites and some chernozems can be restored by alternate wetting and drying, but most other soils do not benefit even if humus is abundant. Plates II*b*, III*a* and *b* show the dried aggregates, the soaked aggregates, and the water-stable crumbs at the conclusions of the experiment on five soils.

It was thought that the humus failed to cement the soils because it was not sufficiently mobile to form a film around the soil particles even after prolonged incubation with soil micro-organisms.

When 0·5 N. NaOH or NH_4OH was added to the soils overnight the humus was dispersed. After drying at 50° they were moistened with a slight excess of hydrochloric acid to fix the films of humates. Clods of soil thus treated were found to be water-stable, whereas lumps that had been treated previously with hydrogen peroxide remained unstable after treatment with alkali then acid. It is difficult to see how humus is similarly solubilized in field soils so that films are formed around soil particles, but diffusible gums might do this. It is conceivable that small quantities of ammonia liberated in the vicinity of ammonifying bacteria might temporarily disperse nearby particles of humus. Films of NH_4 humate might be formed locally and subsequently be precipitated either by H^+ or Ca^{++} ions. Again, it is not known how much earthworms or other members of the soil fauna solubilize soil humus in their intestines during alkaline digestion.

2. *Sterilized soil as a source of food for aggregating organisms.* An experiment was designed to find whether the organic matter present in sterilized soil could serve as a nutrient for micro-organisms and thereby improve structure. Fifty-gramme portions of sieved soils (< 2 mm.) from Woburn and Rothamsted were oven-sterilized in plugged tubes at 150° for 4 hours, then inoculated with autoclaved complete mineral solution containing complex mixtures of micro-organisms, involving 66 bacteria, or 33 actinomycetes, or 22 fungi, or all 121 strains together. Some tubes were kept sterile while others were treated with soil inoculum. After 3, 6, and 9 weeks of incubation at 25° tubes were removed for aggregate analysis and the figures for the various treatments are shown in Table 4.

TABLE 4

Aggregation produced by Mixed Cultures of Micro-organisms utilizing Soil Humus

Soil	*Inoculum*	*Mean weight of aggregates > 1 mm./50 gm. soil after incubating*		
		3 weeks	*6 weeks*	*9 weeks*
Woburn sandy loam	Sterile	0·15	0·07	0·04
	Soil	2·26	1·46	0·85
	Fungi	8·83	4·01	2·41
	Actinomycetes	2·10	1·83	2·30
	Bacteria	0·23	0·08	0·25
	Fungi + Actinomycetes + Bacteria	2·34	1·38	1·35
Rothamsted clay loam	Sterile	9·60	9·67	8·20
	Soil	18·80	13·43	11·57
	Fungi	29·03	35·15	41·67
	Actinomycetes	15·25	17·88	29·01
	Bacteria	9·10	11·08	13·00
	Fungi + Actinomycetes + Bacteria	20·33	15·74	13·24

Woburn sandy loam contained less organic matter and clay than Rothamsted clay loam, and also produced fewer stable crumbs. In both soils the aggregating powers of the various inocula were as follows: fungi > fungi + actinomycetes + bacteria = actinomycetes = soil > bacteria = sterile control. It was rather surprising that sterilized soil should support so many micro-organisms capable of improving aggregation, whereas in the previous experiment it was found that soil inoculum did not improve the structure of soils when alternately wet and dried over a period of 14 weeks. It seems likely that sterilization rendered a portion of the natural humus more available to micro-organisms. It should be noted, however, that there was a considerable decline in aggregation after 9 weeks' incubation, and it is conceivable that after 14 weeks most of the nutritive humus would have been consumed.

This experiment prompted a further one to determine whether soils cemented by fixed films of Ca humate increased or decreased in structure after being inoculated with micro-organisms.

3. *Destruction of fixed humates by micro-organisms.* In order to eliminate interference by naturally occurring humus, Griffith subsoil was used and also a synthetic soil consisting of 40 per cent. fine sand (< 0·5 mm.), 35 per cent. of silt from Narellan soil, 14 per cent. of H kaolin, 10 per cent. of Ca bentonite, and 1 per cent. of Na bentonite. Sufficient quantity of NH_4 α-humate (from Reddestone soil) was added to provide 0·75 per cent. in the two soils. After crumbing, the aggregates were dried, and slowly moistened with a complete-minerals solution containing an extra quantity of calcium chloride to precipitate the humus as the Ca salt. The crumbs were next dried and 25 gm. portions weighed into tubes for dry sterilization. The tubes were inoculated with similar mixtures as used for the previous experiment and incubated at 25° for 3 and 6 weeks. The results of the macro-aggregate analysis are given in Table 5.

TABLE 5

Influence of Mixed Cultures of Micro-organisms on Soil Aggregates cemented with Ca-Humate

Soil	*Inoculum*	*Mean weight of aggregates > 1 mm./25 g. soil*	
		3 weeks	*6 weeks*
Synthetic	Sterile	5·35±0·43	6·34±0·57
	Soil	2·87±0·48	4·82±0·62
	Fungi	3·88±0·37	3·63±0·75
	Actinomycetes	5·99±0·41	6·83±0·93
	Bacteria	1·24±0·25	2·77±0·59
	Fungi + Actinomycetes + Bacteria	2·20±0·38	3·12±0·68
Griffith subsoil	Sterile	10·35±0·33	9·03±0·27
	Soil	6·68±0·56	7·29±0·12
	Fungi	6·69±0·43	7·27±0·39
	Actinomycetes	14·12±1·04	6·92±0·62
	Bacteria	7·56±0·73	3·22±0·25
	Fungi + Actinomycetes + Bacteria	7·03±0·66	7·14±0·70

When similar treatments are compared it will be seen that Griffith subsoil was better aggregated by the humate than synthetic soil. Sterile soils maintained their original structure over a period of 6 weeks, but changes occurred in the presence of micro-organisms. Actinomycetes grew well and improved the structure of Griffith subsoil in the first 3 weeks. Fungal hyphae were observed, but there were too few of them to cause further binding. All other treatments caused an appreciable decline in the weight of aggregates. Plate IV illustrates the effect of the various inocula on aggregation of Griffith subsoil after 3 weeks' incubation.

Evidently most of the micro-organisms caused destruction of the sterilized Ca humate cement without producing much hyphae or gums, so that the disaggregating influences outweighed the aggregating effects. In natural soils containing almost permanent crumbs either the humus is not so readily digested by micro-organisms or the humate films are reformed almost immediately.

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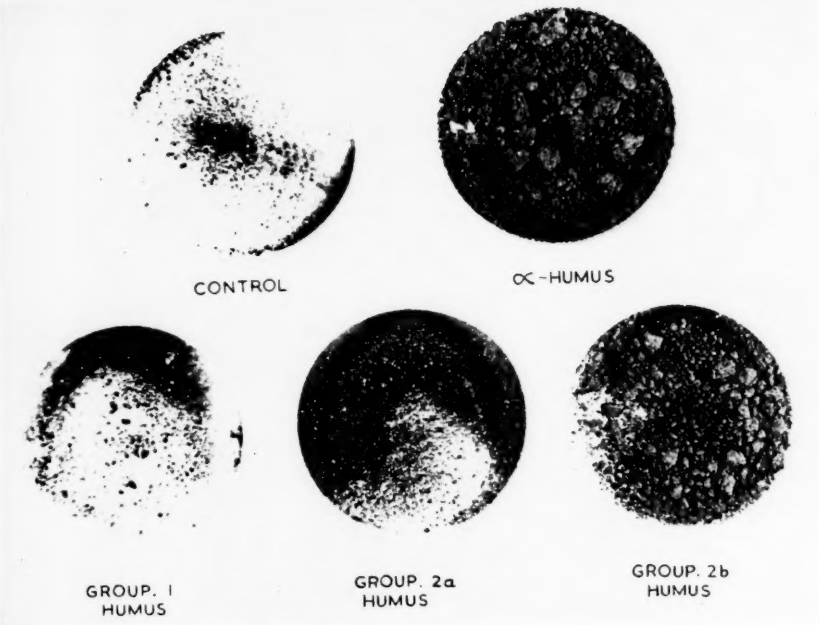
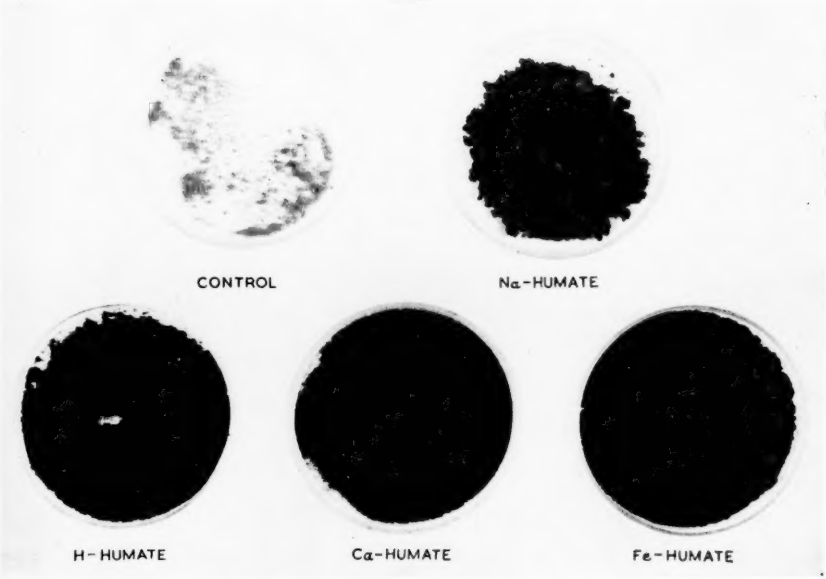
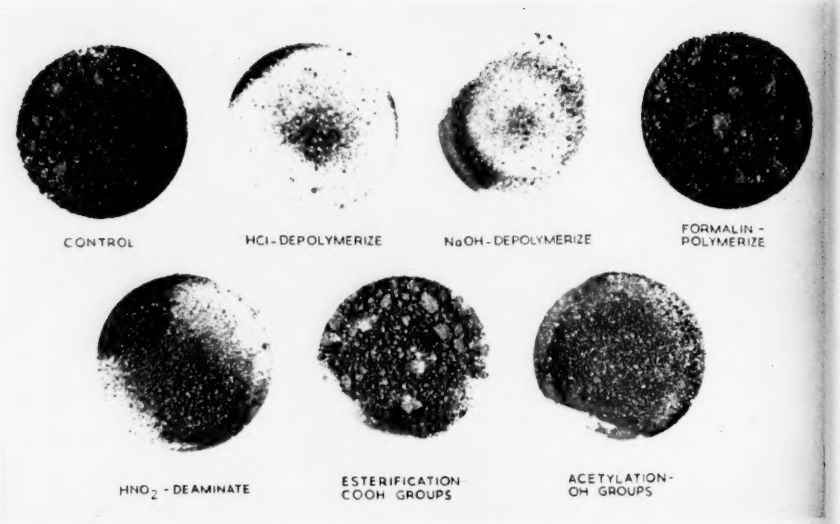


a. Relative cementing power of various humus fractions extracted from Narellan soil.

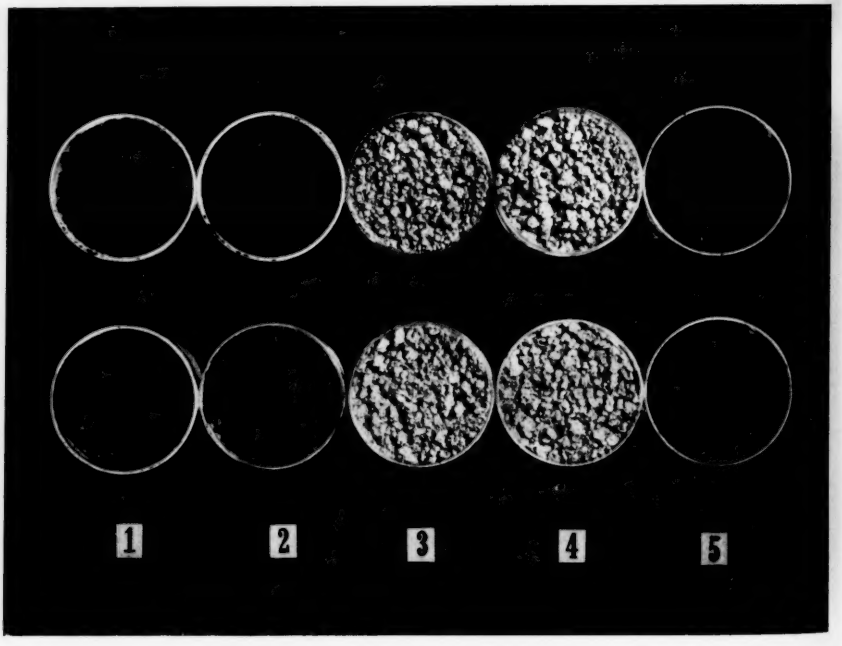


b. Influence of various cations on the cementing power of α-humus from Glen Innes soil.

R. J. SWABY—INFLUENCE OF HUMUS—PLATE I

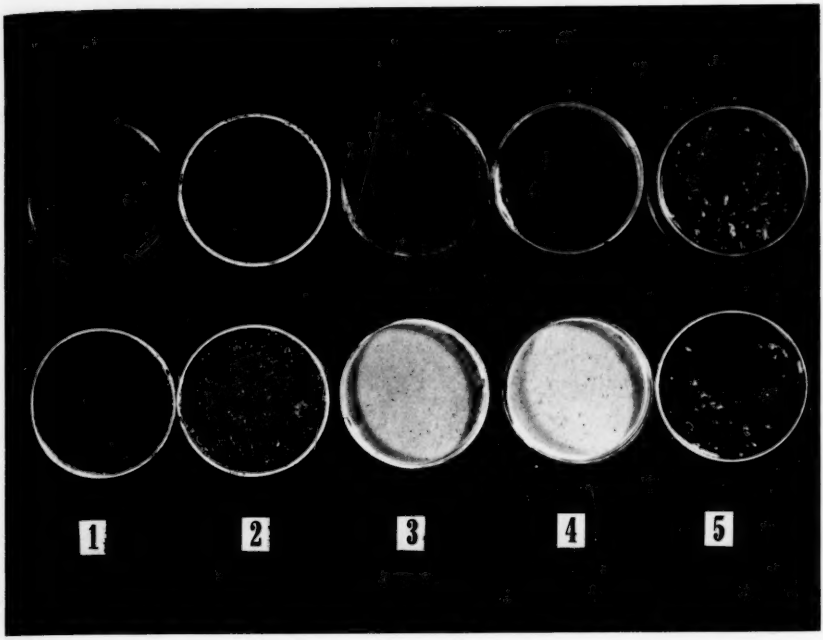


a. Effect of various chemical treatments on the cementing power of *a*-humus.

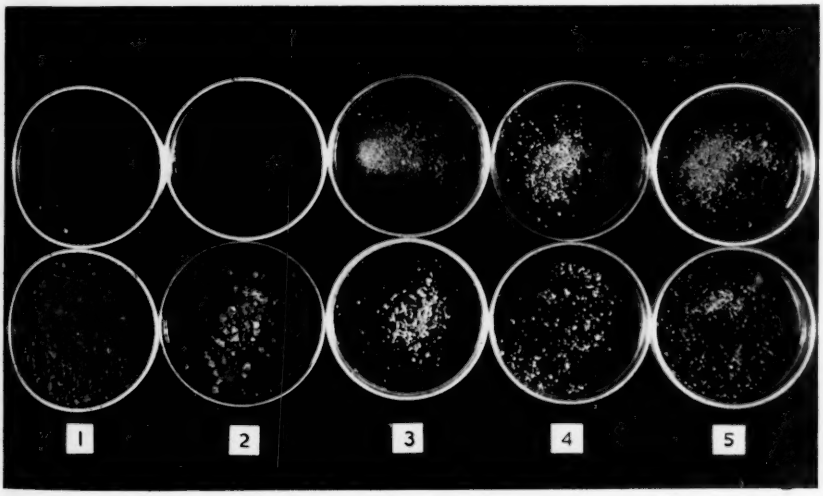


b. Appearance of dried crumbs alternately wetted and dried ten times. (Top line—organic matter present. Bottom line—treated with H_2O_2. 1, Reddestone; 2, Glen Innes; 3, Narellan; 4, Tumbarumba; 5, Griffith.)

R. J. SWABY—INFLUENCE OF HUMUS—PLATE II

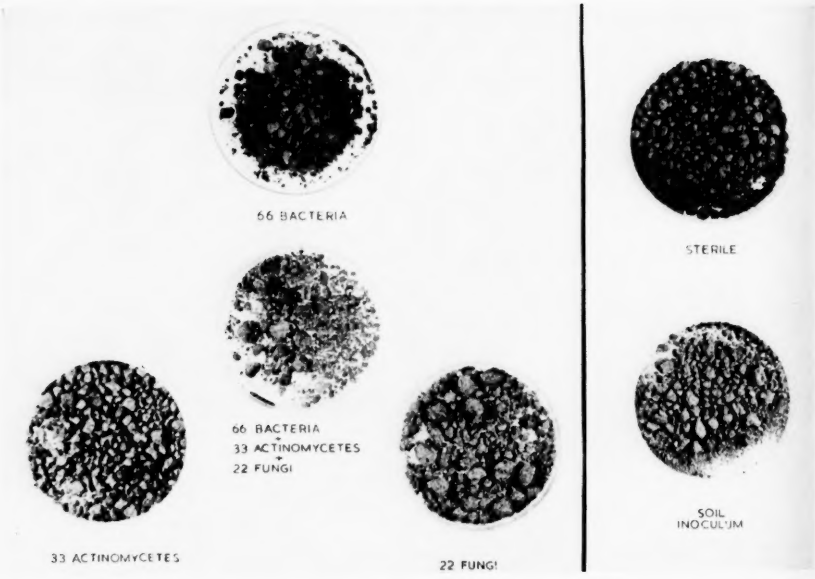


a. Appearance of soil alternately wetted and dried ten times, after flooding with water.



b. Appearance of water-stable crumbs remaining after soils have been wetted and dried ten times.

R. J. SWABY—INFLUENCE OF HUMUS—PLATE III



Influence of mixed cultures on stability of Griffith subsoil cemented with Ca α-humus.

R. J. SWABY—INFLUENCE OF HUMUS—PLATE IV

THE INFLUENCE OF EARTHWORMS ON SOIL AGGREGATION

R. J. SWABY

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WITH ONE PLATE

SINCE the early work of Darwin (1881) showed the importance of earthworms in improving the physical condition of soil, several workers have been interested in the mechanism involved.

Gurianova (1940) found that earthworms greatly aggregated the soil when readily digestible foods were supplied and less so when they were given composted materials. Hopp (1946) and Hopp and Hopkins (1946) added earthworms to sieved soil and found that after 3 days there were twice as many water-stable aggregates as in the control soil. *Lumbricus terrestris*, which produced its own weight of casts in a day, was the most active of the species tested. Dutt (1948) found that casts from a cultivated field were less stable than those from pasture or forest soils. The worm casts were more stable than the natural soil crumbs.

Apart from these few papers there is little information on the mechanism whereby earthworms improve soil structure, so experiments were conducted to clarify the matter.

Experimental Methods and Results

While making observations on the natural structure of grassland and arable soil on Harpenden Common it was noticed that worm casts on permanent grassland were more resistant to the disintegrating action of rain-drops than casts on adjacent arable soil. Fresh casts from *Allolobophora nocturna* and samples of natural soil were collected from the grassland and nearby cultivated land. They were air-dried and 50 gm. of each were subjected to macro-aggregate analysis in the following manner. The samples were soaked in water for 24 hours, transferred to a sieve with 1-mm. holes, and hand-shaken under water 20 times until all fine particles had passed through. The aggregates retained on the sieve were dried at 50° and weighed. The results of this and other treatments are given in Table 1.

It will be seen that earthworm casts from pastures were much more stable than those from cultivated soil. Similarly, natural soil from grassland was better aggregated than that from arable, although not nearly as stable as worm casts derived from soil under pasture. Apparently, both worms and grass roots improve soil structure, and further work was done to explain these effects.

The beneficial effect of the worms did not seem to be due to the cementation of casts by either calcium carbonate or intestinal mucus for, if it were, the casts from both arable and grassland should have been equally stable. It was found that ground-up, dried casts from pasture

TABLE 1

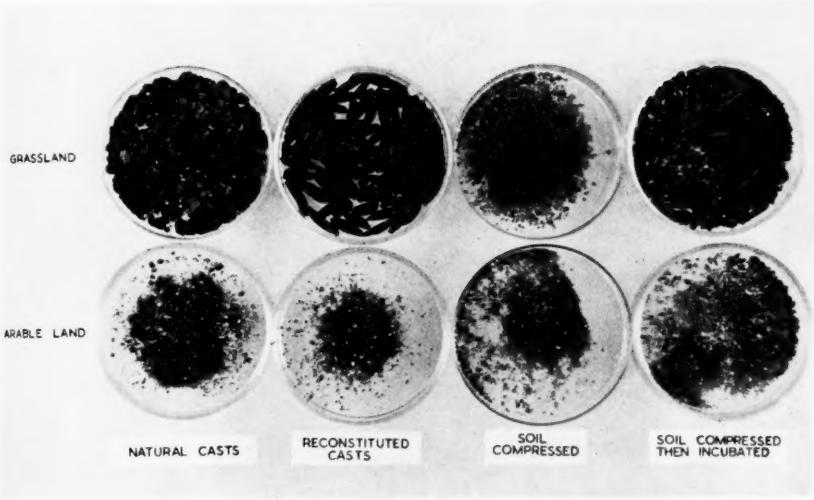
Influence of Various Treatments on Stability of Worm Casts and Moulded Soil from Grassland and Arable Land

Treatment	*Mean weight of aggregates > 1 mm./50 gm. soil*	
	Grassland	*Arable land*
Natural worm casts	42·00	6·40
Natural casts ground then moulded into artificial casts	39·86	4·14
Worm casts incubated 17 days	48·44	3·60
Worm casts incubated 29 days	49·80	4·94
Natural soil	27·22	4·24
Soil ground then moulded into artificial casts	10·84	5·42
Artificial casts incubated 17 days	41·04	5·20
Artificial casts + 0·5% grass roots	9·20	6·46
Artificial casts + 0·5% grass roots incubated 17 days	26·64	23·88

could be moulded by hand, when moistened, into water-stable aggregates, whereas pulverized casts from cultivated land could not be thus reconstituted (Table 1). Evidently, binding substances were derived from the grass roots during passage through the worm. Microscopic examination of fresh casts from pasture revealed the presence of numerous pieces of macerated grass roots and large numbers of bacteria, but very few fungal hyphae. At first it was thought that soil and root fragments were so intimately mixed together in the gizzard of the worm that the casts were merely mechanically reinforced. However, this did not seem to be the real explanation, because thorough mixing of natural grassland soil with root fragments produced only a few stable aggregates (Table 1). Plate and direct* microscopic counts for fungi, actinomycetes, bacteria, and protozoa† were made on both freshly voided casts and soil from the areas under pasture and under cultivation. The only striking differences in microbial counts which could possibly account for the great stability of grassland casts was that they contained many more bacteria than did the other three materials. This suggested that more bacterial gums were produced in the intestine of the worms feeding on grassland soil and that they glued the soil particles together, but these gums were not isolated. Pasture soil was inoculated with a suspension of fresh worm casts, mixed into aggregates, and incubated at 25° for 17 days. After this period the aggregates were wet-sieved and it was found that they had become stabilized, but with fungal hyphae rather than with bacteria (Table 1). It was found that natural worm casts from grassland increased in stability with incubation but those from arable land containing very little nutritive organic matter did not. When soil from either arable or grassland was mixed with 0·5 per cent. of ground grass roots, inoculated with micro-organisms from worm casts, moulded into artificial casts, then incubated for 17 days at 25°, it was found that both treatments became almost equally stabilized. Here, too, fungal hyphae seemed mainly responsible for the aggregation.

* Direct microscopic counts were made by Mr. P. C. T. Jones.

† Protozoan counts were made by Dr. B. N. Singh.



Influence of earthworms and grass roots on stability of soil from grassland and arable land.

R. J. SWABY—INFLUENCE OF EARTHWORM—PLATE I

These experiments indicate that earthworms only improve the structure of soils well supplied with nutritive organic matter. An abundant food-supply increases the number of intestinal bacteria, some of which produce gums and glue the casts into stable aggregates. Under the conditions of restricted aeration inside the earthworm fungi do not flourish. This mechanism for increasing the stability of worm casts differs from that produced directly in soil by the incorporation of readily decomposable material, where the effect of fungal mycelium is more important than that of slime-producing bacteria.

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SOME OBSERVATIONS ON THE OXIDATION OF SOIL ORGANIC MATTER IN THE PRESENCE OF ALKALI

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SHOREY (1930) found that when a soil was treated with alkali oxygen was absorbed and carbon dioxide produced by oxidation of part of the soil organic matter. Since alkali is extensively employed for the extraction of organic matter from soil, the work described in this paper was undertaken to obtain information about the nature and extent of the oxidation of soil organic matter in contact with this reagent. While this work was in progress Chaminade (1946) reported that oxygen has an important effect on the extraction of humic matter from soil by alkali, the amount extracted in the presence of oxygen being as much as three times the amount extracted in a hydrogen atmosphere. This was not found to be the case with the soils used in the work described below.

Experimental

The soils used have already been described (Bremner, 1949*a*; Bremner and Lees, 1949). Oxygen consumption measurements were carried out with the Warburg manometric apparatus, Brodie's solution being used as manometric fluid. The manometers were shaken (110 oscillations per min.) in a water-bath thermostatically controlled at 25° C., 10 minutes being allowed for equilibration before closure of the manometer taps. In the experiments referred to in Fig. 1 and Table 4 alkali was tipped from the side arm of the flask into the main compartment after closure of the manometer taps. When the oxygen uptakes of soils in the presence of fluids other than alkali were measured, potash was added to the inner cup of the Warburg flask to absorb any carbon dioxide produced. The volumes of the flasks and manometer tubes were determined from the weight of mercury required to fill them and flask constants were calculated according to Dixon (1943) and Webley (1947), assuming a soil density of 2. Control thermobarometers were run in all experiments.

Nitrogen was determined by the micro-Kjeldahl procedure already described (Bremner, 1949*a*) and carbon by the method of Van Slyke and Folch (1940).

Results and Discussion

Table 1 gives the amounts of oxygen absorbed in 7 hours by 0·2 gm. samples of Swaffham and Littleport soils in contact with 3 ml. of various reagents. It can be seen that whereas considerable amounts of oxygen are absorbed by soil in the presence of alkali, the amounts absorbed in the presence of neutral reagents are small, indeed negligible.

The oxygen absorbed by a soil/alkali suspension may not be taken up exclusively by soil organic matter since certain readily oxidizable metallic hydroxides (e.g. manganous hydroxide) may be formed on treatment

TABLE 1

The Oxygen Uptakes of Soils in contact with various Reagents

A, Littleport Soil: *B*, Swaffham Soil. 0·2 gm. soil; 3 ml. reagent. Time, 7 hr.

Reagent	*Oxygen uptake* (*mm.*³)	
	A	*B*
0·5 M potassium hydroxide	907	727
0·5 M sodium hydroxide	896	712
0·5 M ammonium hydroxide	205	..
0·5 M sodium carbonate (pH 10·6)	56	71
0·2 M sodium citrate (pH 7·0)	39	58
0·5 M sodium fluoride (pH 7·0)	6	43
0·1 M sodium pyrophosphate (pH 7·0)	7	37
0·1 M sodium pyrophosphate (pH 8·0)	12	..
0·1 M sodium pyrophosphate (pH 9·0)	31	52
Water	8	40

of the soil with alkali. The amount of oxygen absorbed by such hydroxides would, however, be insignificant compared with the amount taken up by soil organic matter.

The oxygen uptake of a soil/alkali suspension varies with the soil (Tables 1 and 3), the alkali (Table 1), and the concentration of the alkali (Table 2). An acid-leached soil takes up more oxygen than the corresponding untreated soil (Table 3).

TABLE 2

The Amounts of Oxygen absorbed in 6 hours by 0·6 gm. Samples of Allotment Soil in contact with 3 ml. of Sodium-hydroxide Solutions of different Concentration

Concentration of NaOH	*Oxygen uptake* (*mm.*³)
0·5 M	214
1·0 M	310
2·0 M	375
3·0 M	398

TABLE 3

The Amounts of Oxygen absorbed in 7 hours by Acid-leached and Untreated Samples of Soil in the Presence of Alkali

Soil	*Oxygen uptake* (*mm.*³)
* Broadbalk	89
* Acid-leached Broadbalk	195
* Allotment	256
* Acid-leached Allotment	351
† Swaffham	709
† Acid-leached Swaffham	874

* 0·6 gm. soil; 3 ml. 0·5 M NaOH. † 0·2 gm. soil; 3 ml. 0·5 M NaOH

The rate of uptake of oxygen by a soil/alkali suspension is greatly affected by shaking (Fig. 1). If the suspension is shaken the rate of oxygen absorption, at first very rapid, decreases slowly with time; if the

suspension is not shaken, however, the relation between oxygen uptake and time is practically linear over the periods for which it has been tested.

Uptake of oxygen by soil/alkali suspensions was found to continue for very long periods. For example, oxygen was still being absorbed by 0·2 gm. of Swaffham soil in contact with 3 ml. of 0·5 M KOH after 5 days. Experiments carried out with the Barcroft–Haldane apparatus

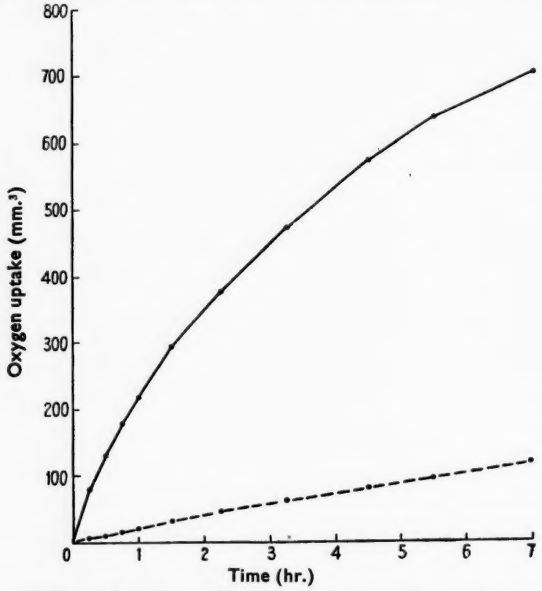

FIG. 1. The effect of shaking on the oxygen uptake of a soil/alkali suspension. 0·2 gm. Swaffham soil; 3 ml. 0·5 M NaOH. ———, shaken; – – –, not shaken.

showed that, calculated on the basis $C+O_2 \rightarrow CO_2$, the amounts of oxygen absorbed at 25° C. in 4 days by 1-gm. samples of acid-leached Hoosfield, Broadbalk, and Allotment soils in contact with 5 ml. of 0·5 M NaOH were sufficient to oxidize 2–3 per cent. of the total carbon in the samples to carbon dioxide. The soil/alkali suspensions were not shaken in these experiments.

Extracts obtained by treating soil with neutral reagents such as sodium pyrophosphate or fluoride contain organic matter that absorbs oxygen when treated with alkali. As Table 4 shows, the oxygen uptake of this organic matter depends upon the concentration of the alkali. Most of it passes into the acid-insoluble (humic) fraction when such extracts are acidified. For example, the humic fraction of a 0·1 M sodium-pyrophosphate (pH 7) extract of Swaffham soil absorbed about six times as much oxygen as did the fulvic (acid-soluble) fraction under comparable conditions.

TABLE 4

The Oxygen Uptakes of Samples of a Neutral Sodium-pyrophosphate Extract of Littleport Soil made Alkaline with Sodium Hydroxide

2·7 ml. samples of extract were treated with 0·3 ml. of NaOH solutions of varying concentration.

Molarity of sample with respect to NaOH	*Oxygen uptake* (*mm.*^{3}) *in 3 hr.*
1·000	572
0·750	544
0·500	510
0·250	356
0·125	202
Nil (control)	0

Table 5 shows the oxygen uptakes of samples of a neutral sodium-pyrophosphate extract of Swaffham soil brought to different pH values by addition of sodium hydroxide. Since pH values were determined with a glass electrode, a saturated calomel half-cell, and a valve potentiometer, it follows that pH values above 10 are unreliable owing to the error of the glass electrode above this pH. It is clear, however, that the oxygen uptake of a solution of high alkalinity (pH $>$ 13) is much greater than that of a less alkaline solution.

TABLE 5

The Oxygen Uptakes of Samples of a Neutral Sodium-pyrophosphate Extract of Swaffham Soil brought to Different pH *Values by Addition of Sodium Hydroxide*

5 ml. samples of extract were brought to pH values shown by addition of NaOH, diluted to 10 ml., and the oxygen uptakes in 5 hr. of 3 ml. samples of diluted solutions determined.

pH of sample	*Oxygen uptake* (*mm.*^{3})
7·0	0
8·0	5
9·0	9
10·0	18
approx. 11	21
approx. 12	57
$>$ 13 *	230

* 5 ml. of extract was treated with 5 ml. of 1·0 M NaOH; pH not determined.

Experiments carried out with neutral 0·1 M sodium-pyrophosphate extracts of Swaffham, Littleport, and Burwell soils showed that, calculated on the basis $C+O_2 \rightarrow CO_2$, the amounts of oxygen absorbed in 7 hours by samples made 0·5 M with respect to NaOH were sufficient to oxidize 1–4 per cent. of the carbon in the samples to carbon dioxide.

Shorey's (1930) observation that carbon dioxide is produced when soil organic matter is treated with alkali was confirmed. For example, it was found that almost 4 per cent. of the carbon in a neutral sodium-pyrophosphate extract of Littleport soil was converted to carbon dioxide when the extract was made 0·5 M with respect to NaOH and allowed to

stand for 6 days. No attempt was made, however, to identify other products of oxidation.

It has been shown in previous papers (Bremner and Lees, 1949; Bremner, 1949*b*) that the amount of organic matter extracted when a soil is treated with alkali increases as the concentration of the alkali and the time of extraction are increased and is greater if the soil is first leached with acid. The results given in this paper show that the oxygen uptake of a soil/alkali suspension is similarly dependent upon these factors (Fig. 1, Tables 2 and 3). Such a relation is to be expected if, as Chaminade (1946) has reported, oxidation of soil organic matter in contact with alkali leads to an increase in the amount of alkali-soluble material. Such a relation would also exist, however, if soil organic matter is oxidized *after* extraction from soil by alkali. Neutral reagents, such as pyrophosphate or fluoride, extract organic matter from soil without uptake of oxygen (Table 1), but separated neutral extracts absorb oxygen rapidly when made alkaline (Tables 4 and 5). By analogy it may be assumed that some of the organic matter extracted by alkaline solutions takes up oxygen after extraction. Although shaking has little effect on the extraction of organic matter from soil by alkali (Bremner and Lees, 1949), it has an important effect on the uptake of oxygen by a soil/alkali suspension (Fig. 1). Since this seemed incompatible with Chaminade's results, the effect of oxygen on extraction of organic matter from acid-leached samples of Hoosfield and Broadbalk soils was tested. Table 6 shows the amounts of organic carbon and nitrogen

TABLE 6

Effect of Oxygen on Extraction of Organic Carbon and Nitrogen from Acid-leached Soils by Alkali

A, extraction carried out in air; *B*, extraction carried out in N_2. 10 gm. soil; 50 ml. 0·5 M NaOH. Time of extraction, 24 hr.

	N extracted (% *total soil–N*)		*C extracted* (% *total soil–C*)	
Soil	A	B	A	B
Hoosfield	35·0	34·7	34·6	34·2
Broadbalk	40·0	39·6	34·4	33·9

extracted in the presence and in the absence of oxygen; in the latter case the extractions were performed in an atmosphere of purified nitrogen and as much air as possible was removed from the soils and alkali before bringing them together. It can be seen that removal of oxygen had no significant effect on extraction. Further experiments showed that practically the same amounts of organic carbon and nitrogen were extracted in a nitrogen atmosphere as in a vigorous current of air. The amounts of humic material extracted, as determined by the method used by Chaminade (1946), and the colours of the extracts were also found to be unaffected by oxygen. The latter observation disposes of any suggestion that the dark colour of alkali extracts of soil is due to the presence of products formed by oxidation of phenolic compounds during extraction.

It is now generally accepted that humus is formed by microbial decomposition of the plant and animal residues that find their way into the soil. Such residues probably contain many substances (tannins, cellulose, &c.) that undergo oxidation in the presence of alkali, but of these only lignin is believed to contribute substantially to soil humus, either in an unaltered or modified condition. Schrader (1922) found that the autoxidation of lignin in contact with alkali led to the formation of alkali-soluble material. A possible explanation of Chaminade's results is, therefore, that undecomposed plant lignin formed a considerable fraction of the organic matter in the soils that he examined.

It appears unlikely that plant lignin is unaltered by microbial processes in the soil. It probably undergoes some oxidation in the processes leading to the formation of soil humus. This would explain many of the characteristics of the lignin-like material of soil. For example, it would account for the solubility of lignin-like material in neutral reagents such as pyrophosphate or fluoride; oxidized lignins disperse at a lower pH (4–6) than unoxidized lignins (Perrenoud, 1943). It would also explain the results of Gottlieb and Hendricks (1945), who applied to soil organic matter the methods recently devised for the study of lignin. The conclusions they reached may be summarized as follows:

1. The material derived from plant lignin in the soil is drastically altered in the kind and position of the peripheral groupings on the aromatic rings.
2. If lignin-like materials are present in soil organic matter, a large percentage of the original hydroxyl groups in the lignin molecule are absent and carboxyl groups have appeared.
3. Soil preparations bear a striking resemblance to alkali lignin in their behaviour to hydrogenation.

Such results are not surprising if plant lignin is modified by microbial processes in soil; the phenolic hydroxyl groups of the lignin molecule are probably susceptible to microbial oxidation. This microbial modification and oxidation of lignin in the soil may proceed far enough to make the amount extracted by alkali independent of further oxidation by oxygen in alkaline solution although further oxidation may occur after extraction. On the other hand, lignin from plant materials recently added to soil may undergo sufficient autoxidation in the presence of alkali to allow the amount of alkali-soluble organic matter to increase steadily in the presence of oxygen, as Chaminade found.

Summary

1. The oxygen uptake of a soil/alkali suspension varies with the soil, the alkali, and the concentration of the alkali; it is greater if the soil is first leached with acid.

2. Absorption of oxygen by soil/alkali suspensions continues for very long periods. The rate of oxygen uptake is greatly increased by shaking.

3. Little or no uptake of oxygen occurs when soils are treated with neutral reagents such as sodium pyrophosphate or fluoride, but extracts obtained by the use of such reagents contain organic matter that absorbs

oxygen rapidly when treated with alkali. Most of this organic matter passes into the acid-insoluble (humic) fraction when such extracts are acidified.

4. With the soils tested, oxidation of soil organic matter in contact with alkali did not lead to an increase in the amount of alkali-soluble material.

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SOME OBSERVATIONS ON GLEYING

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Most of the early references to gleying in soils are confined to profile descriptions. Chemical analyses of such profiles have been reported, but these contribute little to an understanding of the mechanism of the gleying process.

Although it has long been known that micro-organisms play an important part in pedological processes of many kinds, it is not clear when it was first realized that gleying is caused by a microbial reduction of ferric compounds. Albrecht (1941) discusses the role of calcium saturation and anaerobic bacteria in gleying, and this seems to be the first reference to a microbiological cause of gleying. Albrecht appears to regard the process as necessarily involving the production of hydrogen sulphide. The reduction of sulphates to hydrogen sulphide by *Vibrio desuphuricans* occurs in the soil, and this has been extensively studied, particularly in connexion with corrosion problems (Starkey and Wight, 1945, Butlin, 1949). The production of hydrogen sulphide causes the formation of ferrous sulphide, imparting a dark blue or black colour to the soil. The sulphide rapidly oxidizes on exposure to air, giving yellow-brown ferric compounds. However, this is a special example, very different from the general occurrence of gleying. This aspect of gleying has not been considered here.

Allison and Scarseth (1942) found that ferric oxide could be removed from soil material by anaerobic incubation in a sugar solution. These authors remark on the connexion between this process and those of gley and podzol formation.

Roberts (1947) studied the abilities of various micro-organisms, including yeasts and actinomycetes, to reduce ferric oxide, and found that only cultures of *B. Polymyxa*, which he isolated from soil, were effective.

As the experiments described by Allison and Scarseth appeared to offer a convenient method for a laboratory study of the gleying process, the investigation was started along those lines.

Experimental

The soil materials used in this study were: Red-brown clay from the Clay with Flints, Rothamsted; London Clay from Bradwell Waterside, Essex; Gault Clay from Shenley, Bucks.

The experiments were performed on a variety of gleyed soils using glass-stoppered bottles as reaction vessels. These were completely filled with sugar solution before insertion of the stoppers, to obtain anaerobic conditions. In such experiments a vigorous evolution of gas commenced after 2 or 3 days' incubation, and bleaching of the clay was usually apparent shortly afterwards. Frequently the escaping gases loosened the stoppers sufficiently for air to enter, allowing oxidation to proceed with the development of a red-brown coloured solution. In some

instances oxidation was accompanied by the formation of a rust-coloured scum on the surface of the liquid. If oxidation did not take place, however, the solution remained colourless. The fermented solutions invariably contained considerable amounts of iron, although the nature of the organic products appeared to vary to some extent in different fermentations.

The fermentation did not appear to require completely anaerobic conditions in order to produce a gleying effect, as the process has been carried out successfully in test-tubes simply plugged with cotton-wool. The fermented solutions were always coloured dark red-brown, and precipitation of ferric compounds usually, although not invariably, occurred.

The colour of the clay, after complete gleying under anaerobic conditions, varied to some extent with the nature of the clay; for example, the Rothamsted clay was bleached almost white, while London Clay, originally dirty brown, became slate grey. There was little apparent colour change in clays which were originally grey, e.g. Gault or Lias, although the solution of iron was as great as in the former examples. In the dry powdered state the gleyed London and Gault Clays appeared very little darker than the corresponding Rothamsted material, in spite of their great differences when moist.

It is difficult to account for the difference in colour between the gleyed clays; apparently it is not due to differences in the microbial population. This was shown by inoculating sterile suspensions of Rothamsted and London Clays, respectively, with London and Rothamsted enrichment cultures. The colours of the clays were then no different from those obtained when they were subjected to fermentation by their own microflora. This suggested that the grey colour was due to some constituent present before gleying took place, and that separation of the clay into fractions of different particle size might provide a means of concentrating the colouring material. Accordingly Gault and Lias clay fractions (2 μ and less average particle diameter) were separated into fractions, using a Sharples supercentrifuge. It was found in both cases that while the fraction of largest particle size was almost white, the colour darkened with decreasing particle size to intense black in the smallest fraction. X-ray analyses of the Gault fractions revealed no differences in the clay minerals to account for the colour difference, and the only factor suggested by chemical analysis was a relatively large increase in the small organic-carbon content of the fractions:

Percentage Organic Carbon Content of Clay Fractions. Gault Clay

(In order of decreasing particle size)

1	2	3	4
0·20	0·28	0·33	0·39

A similar separation of the London Clay showed no appreciable colour difference between the fractions, all being uniformly brown. If these fractions were treated with hydrosulphite to remove amorphous ferric compounds, the gradation in colour from white to dark grey or black become apparent.

When the London Clay was incubated in a sugar solution and separated

into fractions, the same variation from white to black was obtained. On the other hand, fractionation of gleyed Rothamsted clay (the only material found to give a white residue on gleying) gave uniformly white fractions.

It would appear, therefore, that the colour produced by gleying under these conditions is due to the removal of the masking effect of amorphous ferric compounds.

Variation of pH

In these fermentation experiments the pH of the solution fell to quite low values, usually between 4 and 5; Allison and Scarseth record values

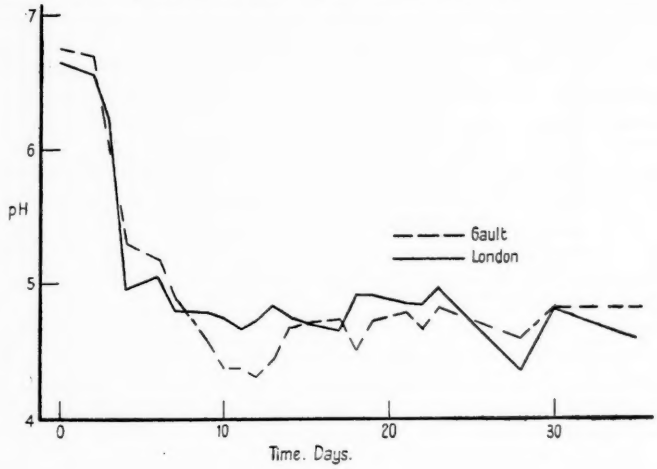

FIG. 1.

as low as 3. To determine how the pH varies throughout the process, a number of fermentations were carried out under conditions that permitted periodic measurement of the pH without disturbance of the system. Tall 400-c.c. beakers were used as reaction vessels. Each beaker was fitted with a bung carrying a glass electrode, an agar-KCl bridge, an overflow, and a vent tube for use during filling. A sterile glucose-peptone medium was prepared, heavily inoculated with a suspension of gleyed material, and sufficient of this mixture introduced into each beaker to fill it completely on inserting the bung. The vents were then sealed, all the joints waxed, and the pH measured at intervals over a period of one month, against a saturated calomel electrode. The overflow tubes dipped under mercury throughout. The results for London and Gault Clays, shown graphically in Fig. 1, show that after an initial rapid fall in the first 4 or 5 days there are comparatively minor changes for the rest of the period.

Rate of Reduction and Bacterial Growth

In order to investigate the connexion between the rate of gleying and bacterial growth, fermentations were conducted under conditions

permitting periodic aseptic withdrawal of samples for analysis. The reaction vessel was a flat-bottomed flask, near the base of which a short tubule was fused; this was sealed with a rubber vaccine cap. The neck of the flask was fitted with a bung carrying a mercury trap and a delivery tube reaching nearly to the surface of the liquid.

The sterile medium and the clay suspension were introduced into the previously sterilized flask, the bung inserted, and the air above the liquid replaced by nitrogen. The joints and vaccine cap were then waxed and the fermentation allowed to proceed at room temperature. Samples were withdrawn, at daily intervals, through the vaccine cap with a hypodermic syringe, the wax coating being renewed each time. The evolution of gases during the fermentation caused a slight positive pressure in the flask, so that there was no danger of air entering through the trap during sampling, unless a very prolonged series of measurements was being made.

The rate of bacterial growth was followed by determining the residual glucose, and the rate of the gleying process by measuring the concentration of dissolved iron in the solution. Glucose was estimated, after removal of protein, &c. (Doak, 1939), by the method of Munsen and Walker. Iron was determined colorimetrically with $\alpha\alpha'$ dipyridyl after evaporation with nitric and sulphuric acids to destroy organic compounds.

Originally, duplication of results was not very good, no doubt largely because of the diversity of micro-organisms in the parent clay. Consistent results could not be obtained by using pieces of clay taken from the same lump as inoculant, and enrichment cultures prepared from gleyed material frequently failed to give any gleying reaction; at best the results were very variable.

To minimize this variability, comparative experiments were made concurrently, using as inoculant aliquots of an aqueous suspension of clay which had been previously incubated for several days. By adopting this procedure agreement was obtained within a series of comparative experiments, but certain discrepancies between series still occurred.

Figs. 2 and 3 show typical results obtained with the London Clay in a medium of composition: glucose 1 per cent., K_2HPO_4 0·1 per cent., NH_4Cl 0·1 per cent., $MgCl_2$ 0·1 per cent., Difco yeast extract 0·02 per cent, clay *c.* 1 per cent. In an attempt to maintain a higher pH throughout the fermentation, an excess (1·5 per cent.) of calcium carbonate was added in one of these experiments (Fig. 3). In this case the pH of the solution after 18 days was 5·0, while the corresponding value without carbonate was 4·2, indicating that the addition did little to simulate soil conditions more closely.

Considering only those features of Figs. 2 and 3 which have been found common to all similar experiments, the following observations may be made:

1. Both the iron and sugar curves are of a sigmoid type, as is the case in bacterial processes. The lag periods are comparable, and they reach their maxima at the same time.

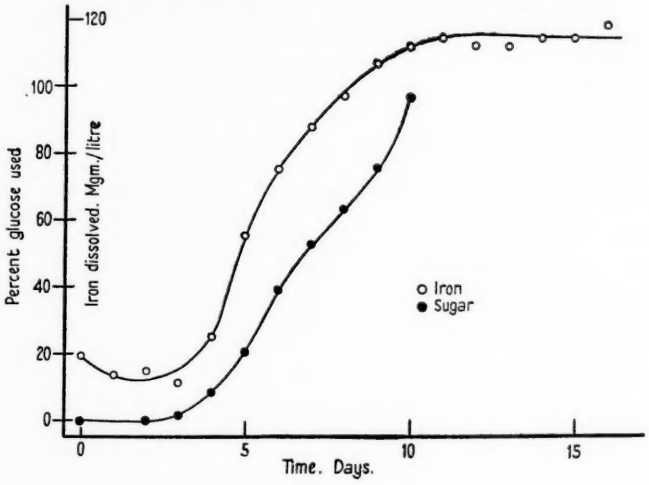

FIG. 2.

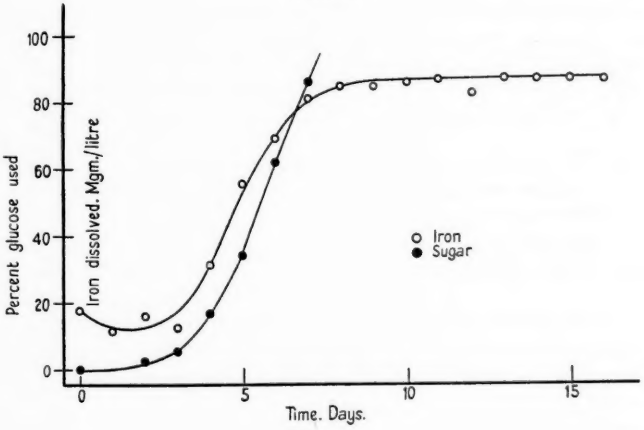

FIG. 3.

2. The rate of assimilation of the sugar is greater in the presence of excess carbonate.
3. The amount of iron dissolved is decreased by the presence of calcium carbonate.

A notable feature of the fermentations carried out in the presence of calcium carbonate was a pronounced formation of gum which formed a slimy clot with the clay and carbonate. Gas bubbles were trapped in the mass which consequently floated on the surface of the liquid. The gum appeared to exert a mechanical effect in slowing down the reaction between the carbonate and the acid fermentation products, for during

the active stages of the fermentation the pH of the solution was usually little higher than where no carbonate had been added.

Acidification with dilute acid destroyed the slimy nature of the clay-gum mixture, and addition of alcohol to the solution obtained after removal of clay gave a white precipitate of the gum. Solutions fermented in the absence of calcium carbonate did not give precipitates of the gum when treated with a calcium solution.

The constitution of the gum is being further investigated.

Previous workers (Zavalishin, 1928, and Ignatieff, 1941) have reported that in gleyed horizons the soil solution contains little or no ferrous iron, whereas significant amounts are obtained by extracting the clay complex with weakly acid solutions. It was therefore thought desirable to determine how much ferrous iron is associated with the clay in the fermentations considered here. Accordingly, approximately 5 gm. of London Clay were incubated in the medium previously described (without added carbonate) for 3 weeks; the clay was then separated from the solution and washed twice with water. The ferrous iron content of the combined solution and washings was determined as before. The clay was extracted with 0·1 N hydrochloric acid until no further ferrous iron was removed, and the iron content of the extract determined. Neither the solution nor the clay extract gave a reaction for ferric iron with thiocyanate. Finally, the residual iron content of the clay was determined after evaporation with hydrofluoric acid and fusion of the residue with potassium bisulphate. The results are given below:

Mgm. ferrous iron in solution	106
„ „ associated with the clay . . .	12
Hence percentage of total iron associated with the clay .	10
Residual iron content of the clay (as percent. Fe_2O_3) .	3·2
Original „ „ „ „ „ .	10·3

The final pH was 4·1.

Thus by far the greater part of the reduced iron appeared in the solution.

Up to the present it has not been possible to obtain pure cultures of any of the micro-organisms responsible for the processes described in this paper; it is hoped that these will be available at a later date.

Discussion

As a criticism of the methods employed in this work it may be said that the conditions are almost certainly more drastic than those likely to obtain naturally. For example, gleyed horizons do not usually have pH values lower than 5, and values higher than this are common. In view of this, deductions made from fermentation experiments concerning, in particular, the fixation of ferrous iron by the clay, are unlikely to be valid for field conditions. Also, the laboratory experiments were made on closed systems in which leaching and diffusion of solution products, which must be considered in the field, play no part.

The existence in solution of ferric iron at pH values as high as the experimental values quoted here argues the formation of complex ions with the organic products of the fermentation; the intense colour of the

oxidized solutions is confirmatory evidence for this assumption. Butyric acid, which has been detected in many of the fermented solutions, as well as many of the aliphatic acids which might be formed under the conditions employed, are known to give complexes with ferric iron (Treadwell, 1935). The observation by Ignatieff that the ferrous iron content of a gleyed soil is increased by exposure to sunlight, recalling the well-known photochemical reduction of, for example, ferric oxalate, is of interest in this connexion. No clear evidence of the existence of ferrous organic complexes in the fermentation solutions has been obtained in the few tests which have been made; the subject of complex formation is under investigation.

Although, as has been mentioned, objections may be made against a rigorous application of these results to gleying as a natural phenomenon, they afford a ready explanation for the common appearance of bleached surfaces along natural fissures in incompletely gleyed horizons. Presumably organic matter carried by rain water tends to pass preferentially along such fissures, and provide an energy source for micro-organisms at the surface of structural elements. Gleying would thus commence at these surfaces, and gradually extend into the elements. If it is not assumed that significant amounts of iron pass into the soil solution on gleying, it is difficult to visualize how such profiles are formed.

Summary

When a clay is gleyed artificially in a sugar medium, the pH usually falls to a value between 4 and 5. A gum is often formed when calcium carbonate is present.

Most of the iron reduced is present in the fermented solution, only a small fraction being associated with the clay. On oxidation, the fermentation solutions do not invariably give precipitates of ferric compounds as occasionally ferric organic complexes are formed.

The author wishes to thank Dr. A. Muir, who suggested the problem, for his helpful advice and criticism.

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THE ESTIMATION OF FREE IRON OXIDES IN SOILS AND CLAYS AND THEIR REMOVAL

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THE estimation and removal of the free iron oxides present in soils are of considerable interest in view of the importance of iron oxides in the process of podzolization, laterization, and phosphate fixation. The removal of free iron oxides also facilitates the identification and estimation of minerals present in soils and clays by X-ray, petrographic, and thermal analyses.

A number of methods has been suggested since Tamm (1922) first proposed acid ammonium oxalate to remove free oxides of silicon, aluminium, and iron. Mattson (1931) used hot saturated aluminium chloride to remove the free sesquioxides from clays. Drosdoff and Truog (1935) found that when soil or clay suspensions were saturated with hydrogen sulphide under alkaline conditions, free iron oxides were converted into sulphides which could subsequently be removed by 0·05 N hydrochloric acid. This treatment dissolved finely ground ferric oxide, but had no appreciable effect on the iron in biotite, basalt, and granite. Truog and co-workers (1936) later modified the method. Instead of passing hydrogen sulphide through the suspension, nascent hydrogen sulphide was produced within the suspension by the action of oxalic acid on sodium sulphide. The iron sulphide was dissolved by the oxalic acid. The aluminium exchange complex was found to be quite stable towards the reagent, but the iron exchange complex was less stable. Jeffries (1941) proposed a method for removing iron oxides from sand and silt for mineralogical estimation. Iron was reduced by the action of nascent hydrogen produced by the action of oxalic acid on an aluminium cylinder immersed in a boiling solution. Dion (1944) modified the method of Jeffries and carried out the reduction by heating the soil suspension with 10 per cent. ammonium tartrate in presence of metallic aluminium. Allison and Scarseth (1942) used anaerobic decomposition of a sugar solution in soil to reduce the iron oxide to the ferrous and soluble state.

The present investigation was carried out in an attempt to find a suitable method or modification of existing methods for estimating and removing free iron oxides from soils and clays without affecting the other clay minerals. With this end in view preliminary experiments were carried out to find the effect of:

(1) Soil-solution ratio,
(2) Time of digestion or shaking,
(3) Effect of repeated treatments,

on the removal of iron oxides by different methods.

The soil used was a subsoil from Knott Wood, Rothamsted. Organic matter was destroyed by the action of hydrogen peroxide and the

exchangeable bases removed by leaching with 0·5 M acetic acid. The soil was then washed with water and dried.

TABLE 1

Iron Oxides removed by Different Methods (expressed in mg.)

	5 gm. soil	*10 gm. soil*
Tamm's Method. Ammonium oxalate + oxalic acid. pH 3·25		
First extraction	4·4	7·3
Second extraction	2·5	5·4
Jung's Method. Sodium tartrate + tartaric acid		
First extraction	2·9	5·0
Second extraction	1·8	3·9
Scarseth and Allison's Method. Anaerobic decomposition of glucose		
First extraction	125	203
Second extraction	74	110
Dion's Method. Ammonium tartrate and Al foil		
Heated for 40 minutes	30	36
Heated for 60 minutes	58	80
Heated for 90 minutes	76	136
Truog Treatment. Na_2S—oxalic acid		
Once treated	217	231
Twice treated	230	300

It will be seen from the results that the amount of iron dissolved varied widely between the different methods and even by the same method it varied with the soil/solution ratio, the time of digestion, and the number of extractions.

In the course of the investigation two new methods of estimating and removing iron oxides came to the author's notice. Dr. Schofield, who had noticed that acid ammonium oxalate reduces iron quite rapidly under the action of sunlight, suggested to the writer that this might provide an easy and satisfactory method for removing iron oxides. The other method is the reduction of iron oxide by sodium hydrosulphite. This method had been used by Galabutskaya and Govorova (1934) in Russia to remove iron oxides from kaolin. A detailed study was therefore made of these two methods, Tamm's method being included for comparison.

Materials

The clay fractions (0·002 mm.) of four soils were separated after destroying organic matter and analysed by the method described in Wright's *Soil Analysis*.

A brief description of soils:

1. Knott Wood. A light yellowish-red clayey subsoil (9–18 in.) from Knott Wood, Rothamsted.
2. Africa. A subsoil (9–18 in.) from a 'black cotton soil', Nyasaland, Africa.
3. Nagpur. A grey decomposed mass at a depth of 13 to 16 ft. developed on basalt at Nagpur, India.
4. Nilgiri. A deep red subsoil (1–3 ft.) from Nilgiri Hills, India.

The chemical composition of the four clay fractions is given in Table 2.

TABLE 2

The Chemical Composition of Clay Fractions

Clay fractions	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	SiO_2/Al_2O_3	SiO_2/R_2O_3
Knott Wood	40·6	24·0	11·7	2·88	2·20
Africa	35·6	26·9	14·1	2·25	1·69
Nagpur	50·5	9·76	12·2	8·78	4·90
Nilgiri	17·8	36·4	27·3	0·83	0·55

Previous detailed study of the clay fractions from Nagpur and Nilgiri by the author showed that the clay from Nagpur consists mainly of montmorillonite with little free sesquioxides and the clay from Nilgiri consists of kaolinite, gibbsite, and iron oxides.

The Acid Ammonium Oxalate-Sunlight Method

Since the acid ammonium oxalate has a very low pH which may have some destructive effect on the clay minerals, the highest pH of oxalate solution at which photo-chemical reduction can take place was investigated. 0·2 M ammonium oxalate and 0·2 M oxalic acid were mixed in proportion of 2 : 1, 4 : 1, and 8 : 1 to obtain pH values of 3·4, 3·8, and 4·2 respectively.

It was observed that the reduction of iron took place more rapidly at the lower pH values. The reaction was slow at pH 4·2. It was found for Knott Wood clay that, though the amounts of iron that came into solution were almost the same at the three pH values, the reaction took more than 10 times as long at pH 4·2 as at pH 3·8. Though the reaction was more rapid at pH 3·4 or below, that at pH 3·8 was not too slow and finally the mixture (4 : 1) with pH 3·8 was adopted as standard for removing the iron oxide.

The method used is as follows:

The clay (0·25–1 gm.) was placed in a centrifuge tube and the oxalate solution (35–40 ml.) added. The tube was then placed in sunlight and shaken occasionally for 2–4 hours. When a straw yellow colour was developed, the suspension was centrifuged and the liquid decanted off. Further oxalate solution was added and the process repeated till the solution remained colourless, under the action of sunlight. If the liquid was left for too long a time in sunlight yellow ferrous oxalate was precipitated in the first two or three extracts. This could, however, be dissolved by hydrogen peroxide and oxalate. It is always preferable to centrifuge the suspension before this occurs. The complete reaction takes 10–20 hours of bright sunlight.

The Sodium Hydrosulphite ($Na_2S_2O_4$) *Method*

Preliminary experiments with hydrosulphite showed that the reaction between ferric oxide and hydrosulphite was slow at ordinary room temperature but became fairly rapid at about 40° C., and the concentration of hydrosulphite over the range 2–5 per cent. did not materially affect the solution of iron, although less time was required with 5 per cent. solution. In later experiments a 4 per cent. solution was used.

Through the decomposition of sodium hydrosulphite to hydrogen sulphite, the reaction of the solution becomes acid. It was found that with 4 per cent. hydrosulphite solution the final pH varies from 2·9 to 3·5. With a view to carrying out the extraction as nearly as possible to neutrality, the reaction was carried out with normal acetate containing 0·2 N tartrate. Tartrate was used to prevent the precipitation or adsorption of ferrous ion at high pH.

In Table 3 the results on the effect of pH on the removal of iron oxide are given.

TABLE 3

The Effect of pH on the Removal of Iron Oxide from Clay Fractions by Extraction with Hydrosulphite (expressed as percentage of Clay)

Clay	*Low pH* 2·9—3·4	*High pH* 5·4—6·0
Knott Wood .	7·6	7·6
Africa . .	9·6	9·4
Nagpur . .	2·2	2·4
Nilgiri . .	26·5	26·8

The results show that the amounts of iron dissolved are independent of the pH of the solution.

The effect of temperatures of 40–2° and 60–1° C. on the removal of iron oxide was next studied. At the lower temperature the clay from Nilgiri appeared to bleach after 8–10 minutes' treatment and complete bleaching was effected in 30–40 minutes, whereas at 60–2° C. the bleaching started after 2–3 minutes and after 5 minutes the clay turned to a black mass, due to the formation of iron sulphide. Iron was estimated both in the solution and in the residue by treating the residue with acid ammonium oxalate to dissolve the iron sulphide formed. The results are shown in Table 4.

TABLE 4

Effect of Temperature on the Removal of Iron Oxide by Hydrosulphite (expressed as percentage of Clay)

Temperature	*Duplicates*	Fe_2O_3 *in solution*	Fe_2O_3 *in oxalate*	*Total* Fe_2O_3
40° C	a	26·4	0·05	26·4
	b	26·6	0·07	26·7
60° C	a	11·8	15·5	27·3
	b	10·9	16·5	27·4

The results show that there is very little difference in the total amount of iron oxide brought into solution at these two temperatures. A considerable quantity of ferrous sulphide was formed at higher temperature. This can generally be dissolved by acid oxalate, but with certain clays and soils a small amount of ferrous sulphide is always formed and gives a bluish tinge which is not completely removed by acid ammonium oxalate, but is removed almost completely by 0·02 N hydrochloric acid.

The effect of two subsequent extractions by hydrosulphite was studied with results reported in Table 5.

TABLE 5

The Amounts of Iron Oxide as Percentage of Clay dissolved by Two Extractions with Hydrosulphite

Clay	*1st extract*	*2nd extract*	Fe_2O_3 *in 2nd extract as per cent. of 1st extract*
Knott Wood . .	7·77	0·33	4·0
Africa . . .	9·63	0·31	3·2
Nagpur . . .	2·40	1·00	41·6
Nilgiri . . .	26·6	0·42	1·5

It will be seen from the results that, with the exception of clay from Nagpur, the second extract brought very little iron oxide into solution. This shows that hydrosulphite dissolves almost all free iron oxide present in clays in the first treatment. Montmorillonitic clay minerals containing iron may be partially decomposed by such treatments. Iron which comes into solution in the second and subsequent extractions may be derived from partially decomposed clay minerals and not from free iron oxide. Further evidence that montmorillonitic clay is partially decomposed by such treatment will be given later. Two variations of the hydrosulphite method were used as follows:

To 0·25–1 gm. clay in 100-ml. centrifuge tubes, 50 ml. of water or 50 ml. of normal sodium acetate plus 0·2 N sodium tartrate mixture were added and shaken thoroughly to disperse the clay. Two grammes of sodium hydrosulphite were added and the tube was placed in a water-bath maintained at about 40° C. The suspension was stirred intermittently during the period of extraction which was continued until complete bleaching was reached. Usually this took 30–50 minutes. The suspension was centrifuged and the solution collected for estimating iron. The clay was treated with 50 ml. of 0·02 N hydrochloric acid and shaken thoroughly for 10–15 minutes. After centrifuging the liquid was added to the former solution and iron was estimated by the usual method.

The Solubility of Goethite and Hematite

It was found that both goethite and hematite were completely dissolved by the action of sunlight in presence of oxalate solution, and also by hydrosulphite. The reaction was, however, slow compared with that of iron oxide in clays. The solubility of these minerals in Tamm's solution is, however, negligible.

In Table 6 the results for the amounts of iron oxides removed from clays by different methods are presented.

It will be seen from the table that Tamm's solution dissolves very little iron oxide from clays and that the oxalate-sunlight and hydrosulphite treatments dissolve similar amounts, except for clay from Nagpur. It may be pointed out that 98–100 per cent. of the iron oxide present in

TABLE 6

The Amount of Iron Oxide as Percentage of Clay removed by Different Methods

Clay	*Tamm's method*	*Oxalate-sunlight method*	$Na_2S_2O_4$ *method*
Knott Wood	0·56	8·1	7·6
Africa	0·19	9·5	9·4
Nagpur	0·46	7·1	2·4
Nilgiri	0·73	26·8	26·8

the clay from Nilgiri is dissolved by both treatments. Such results could be expected since this clay contains kaolinite, gibbsite, and iron oxide. Only 68–75 per cent. of iron oxides present in clays from Knott Wood and Africa is dissolved by the treatments. Evidently these clays contain either montmorillonite or hydrous mica minerals. Furthermore, as the two methods dissolve similar amounts of iron oxides from these two clays and the second hydrosulphite treatment brings out very little iron oxide, it may be assumed that the iron minerals other than oxides in these clays are fairly stable. For the clay from Nagpur the oxalate-sunlight treatment dissolves considerably higher amounts of iron oxide than the hydrosulphite treatment. If this clay is subjected to a second or third hydrosulphite treatment, considerable amounts of iron are brought into solution. It is therefore probable that the iron-silicate complex of this clay is not stable towards the reducing agent. Evidence to this effect will be given later.

The Effect of Various Treatments to remove Iron Oxides on the Base-exchange Capacity of Clays

It is generally accepted that free oxides of iron, aluminium, and silicon possess little or no exchange capacity, so the removal of any of these constituents from clays should not alter the base-exchange capacity of the material.

In the present study the base-exchange capacity was estimated both for untreated clays and for the same clays after various treatments for removing iron oxides. The method was as follows:

The clay (0·5–1 gm.) was leached with 200 ml. of N ammonium acetate at pH 7·0 and then with 50 ml. of N ammonium chloride of pH 7·0. Excess ammonium salt was removed by washing with alcohol. The ammonium absorbed was displaced by N potassium sulphate at pH 2·0 and ammonia estimated in solution. The results are given in Table 7.

The results show that with Tamm's treatment the exchange capacity increased in three clays, the increase for clay from Nilgiri being about 33 per cent. of the original. It has often been suggested that the increase in exchange capacity is due mainly to the removal of ferric oxide which had physically blocked the exchange spots. This explanation is, however, hardly applicable in these clays. Three clays which showed an increase in exchange capacity after Tamm's treatment contain a large

TABLE 7

The Base-exchange Capacity of Clay Fractions Before and After Various Extractions (expressed as m.e. per 100 gm.)

Clay	*Untreated*	*Tamm*	*Oxalate-sunlight*	$Na_2S_2O_4$ *pH* 2·9–3·4	$Na_2S_2O_4$ *pH* 5·4–6·0
Knott Wood	47	48	44·3	49	46·6
Africa	30	32	29·0	32·6	30·6
Nagpur	80	78	68·5	77	78·0
Nilgiri	6·4	8·5	8·3	8·4	8·1

amount of free iron oxides as shown by other treatments, but Tamm's treatment brought into solution only a very small fraction of the free oxides (Table 6). This small fraction could not appreciably alter the physical blocking, especially as no proportional increase was noticed by the more effective methods of removing iron oxides. The suggestion is therefore put forward that the increase in the exchange capacity is due to either one or both of the following reasons:

1. Removal of 'fixed exchange' iron or aluminium.
2. Removal of $Al(OH)_2^+$ from the outer edges of the crystal lattice.

The term 'fixed exchange iron' is used to denote iron which occupies an exchange position as FeO^+ which is no longer exchangeable by salt solution. That iron exists in such forms has been suggested by Dion (1944). The 'fixed exchange iron' may be partly or wholly soluble in Tamm's reagent. Only a small amount of such 'fixed exchange iron' need be assumed to account for the increase in the exchange capacity observed by Tamm's treatment. But Tamm's reagent may also dissolve a small amount of $Al(OH)_2^+$ from the outer edges of the crystal lattice.

The kaolinite structure contains alternate silica and alumina sheets, whereas in montmorillonite structures the alumina sheet is sandwiched between two silica layers. In the former type therefore more alumina will occur at the surface than in the latter type. The possibility of removal of $Al(OH)_2^+$ by simple solution is therefore greater in kaolinite than in montmorillonite. Since increase in exchange capacity of clays after various treatments has generally been observed to be greater in the kaolinitic clays, the possibility exists that the increase may be due at least partially to the removal of surface aluminium.

The exchange capacity of the clay from Nilgiri was increased by all treatments. This is probably due to both of the above reactions.

The exchange capacities of three clays were decreased by the oxalate-sunlight treatment, the decrease being fairly high in the clay from Nagpur. The small decrease in the case of clays from Knott Wood and Africa is probably due to slight breaking of the crystal lattice by prolonged action of the reagent. The montmorillonitic clay from Nagpur has been decomposed considerably by the treatment.

The results of hydrosulphite treatments at two pH levels (2·9–3·4 and 5·4–6·0) are interesting. After treatment at higher pH level, the exchange capacity remained practically unaltered in Knott Wood and the African clays, but, curiously enough, the exchange capacity increased

after extraction at lower pH levels. It might have been expected that the higher acidity would have decreased the exchange capacity through a partial decomposition of clay minerals. The increase in exchange capacity can, however, be explained by the removal of surface $Al(OH)_2^+$ at the lower pH level. There was a reduction in the exchange capacity of Nagpur clay after both treatments through the partial decomposition of clay minerals (montmorillonite).

An experiment to find out the effect of successive hydrosulphite treatments on the base-exchange capacity for Nagpur and Knott Wood clay fractions was carried out and the results are reported in Table 8.

TABLE 8

The Effect of Repeated Extractions with Hydrosulphite at two pH Levels (2·9–3·4) and (5·4–6·0) *on the Amounts of* Fe_2O_3 *removed and the Base-exchange Capacity of Clay Fractions*

Treatment	*Nagpur*				*Knott Wood*			
	Iron oxide removed %		*Base-exchange capacity m.e. per 100 gm.*		*Iron oxide removed* %		*Base-exchange capacity m.e. per 100 gm.*	
pH	2·9–3·4	5·4–6·0	2·9–3·4	5·4–6·0	2·9–3·4	5·4–6·0	2·9–3·4	5·4–6·0
Before	..	..	80	80	..	..	47	47
1st	2·2	2·4	77	78	7·6	7·55	49	46·6
2nd	1·15	0·95	75	72	0·21	0·30	49	46·2
3rd	0·90	1·0	69	64	..	..	..	..

The results show that the montmorillonitic clay from Nagpur is not stable towards the reducing action of hydrosulphite at both pH levels, the exchange capacity of the clay being progressively reduced by the successive treatments. It may be pointed out that there is smaller reduction in the exchange capacity at lower pH level by the second and third treatments than at the higher pH level. It is probable that at the lower pH level the observed exchange capacity is the result of two opposing factors, namely, a decrease due to breaking of the crystal lattice and an increase due to the removal of surface $Al(OH)_2^+$. At the higher pH level the observed exchange capacity is due to the breaking of the crystal lattice only. In Nagpur clay considerable amounts of ferric oxide in comparison with the first extract also came into solution by the second and third extracts. Iron coming into solution in the second and third extracts is evidently from the partially decomposed montmorillonite and not from free iron oxides. In Knott Wood clay the second hydrosulphite treatment brought very little iron oxide in solution and there was no reduction in the base-exchange capacity. Evidently the treatments do not affect the clay minerals which are probably mainly hydrous mica.

Conclusion

The results of the present study clearly demonstrate that no method is quite satisfactory for removing free iron oxides without affecting the

crystal structure, but the hydrosulphite method has proved superior to other methods. Its merits may be summarized as follows:

1. Efficient removal of free oxides.
2. Less destructive affect on clay minerals.
3. Easy and quick manipulations.

The study of the base-exchange capacity as affected by different methods of extraction of iron oxides has thrown some light on the difference in stability of various clay minerals towards reducing agents. Thus

1. Kaolinitic minerals are quite stable towards reducing agents.
2. Hydrous mica or illite is also fairly stable.
3. Montmorillonite containing iron is not stable towards the reducing agents.

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THE RETENTION OF PHOSPHATE BY SOIL. A REVIEW

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THE scope of the present review is limited to the evidence for, and the nature of, the retention of phosphate by soil. It does not include the numerous experiments that have purported to measure the availability to plants of the retained phosphate. The literature up to 1932 has been surveyed by Weiser (157) and some of the more recent literature by Midgley (95).

The following terminology will be adopted:

'Phosphate' refers to the anions which are formed from the dissociation of orthophosphoric acid or any of its salts.

'Phosphate sorption' and 'phosphate retention' are used synonymously and are taken to mean the removal of phosphate from solution by soil or by a soil constituent. No particular mechanism is implied.

'Phosphate adsorption' and 'phosphate absorption' are taken to mean the retention of phosphate at a surface, and within a solid phase, respectively.

'Phosphate fixation' is used to describe any change that the phosphate undergoes in contact with the soil, which reduces the amount that plant roots can absorb. It is understood that plant roots active in nutrient absorption can penetrate into the locality of the phosphate, that is, the phosphate is not positionally unavailable to the roots.

There is, unfortunately, a general lack of agreement on the meanings that should be associated with these terms, especially with 'phosphate fixation', which is more commonly taken to mean the retention of phosphate from solution. As the retention of phosphate by soil and its decreased availability to plants are two processes that have quite different implications in agriculture, and in addition probably differ chemically, it is desirable to distinguish between them. This is done by using the above terminology.

General

The retention of phosphate by soil seems to have been first demonstrated by Way (153) in 1850, though Liebig (71) had anticipated the results 10 years earlier. Liebig stated, with regard to soluble phosphates, that 'in a few seconds the free acids unite with the bases contained in the earth, and a neutral salt is formed in a very fine state of division'. Way (153) found that the whole of the phosphate was retained when solutions of sodium phosphate in water, and guano in dilute sulphuric acid, were poured over a layer of calcareous soil. He thus found that a solution of phosphate differed from solutions of nitrate, chloride, and sulphate which passed through the soil with their concentrations un-

changed. Way suggested that an insoluble calcium phosphate was formed. The importance of his observation was that water-soluble phosphate, as in the fertilizer superphosphate which was then coming into use, was retained by soil and not leached out in the drainage water. This was confirmed by Way when he carried out analyses of drainage water and found only small amounts of phosphate (155). In three of the seven samples he examined the amount was too small to determine. Subsequently, many similar determinations have been carried out and in general they yield the same result.

Some losses have, however, been reported. Robinson and Jones (119) carried out analyses of 6 soil profiles 10 years after the soils had been given a broadcast application of basic slag (200 lb. P_2O_5 per acre). They could find little trace of the phosphate and concluded that it had been washed out of the top 18 in. of the soil by the heavy rainfall (35–75 in. per annum at the 6 centres) within 6 to 10 years after application. Some workers have reported losses from sandy soils (34, 81, 102), and others from soils receiving unusually heavy phosphate applications (61). Glentworth (53), observing that total phosphate is lowest and acetic acid-soluble phosphate is highest in the gley horizon of poorly drained soils, suggests there might be a loss of phosphate in the ground water of poorly drained soils. Loss of phosphate may be serious where there is much run-off water (8, 64, 120, 127).

Apart from these special circumstances most of the phosphate remains in the soil. Its distribution within the soil is, however, of importance, because the phosphate should penetrate into the root zone of plants if it is to be of any value for crop growth. Way (154) and Voelcker (147) assumed that the water solubility of superphosphate should ensure not only the formation of a finely divided precipitate in soil, but also its adequate distribution within the soil. It has, however, been shown by a number of workers (8, 23, 24, 55, 58, 90, 104, 146, 150) that movement of phosphate within the soil is sometimes limited to as little as 2 or 3 in., though it varies according to soil texture, amount of phosphate applied, rainfall, &c. Dyer (39) analysed the continuous-wheat plots at Rothamsted and found that most of the phosphate that had been applied, and had not been removed in crops, was still present in the top 9 in. of soil. The penetration was greater when other fertilizer salts or farmyard manure had been used in conjunction with the superphosphate. This effect of organic matter has also been observed by others (43, 47, 91). Stephenson and Chapman (136) found evidence for the penetration of phosphate below the first foot in medium-textured and light soils, but for practically no penetration below 6 in. in heavy soils. Phosphate that has been broadcast on a soil growing grass seems to move only very slowly from the surface (12, 94, 128, 132, 160, 162), though Doak (35) found appreciable penetration to 4 in.

According to Weaver (156) some plants such as cereals and swedes may not send many roots into the top inch or two of soil. It is therefore not surprising that under some conditions at least the smallness of the movement of phosphate within the soil is responsible for the low response of crops to a phosphate application (24, 60, 94).

A. *Factors affecting Phosphate Retention*

1. *Mechanical composition of soil*

It is generally accepted that most of the retaining power of soil for phosphate lies in its finer mechanical fractions, especially clay. Hibbard (59) found that the retention of phosphate by the three fractions that were retained on 1-mm., 40-mesh, and 100-mesh sieves, and the fraction that passed through a 100-mesh sieve was greatest with the finest fraction and decreased as the particle size increased. Perkins, Wagoner, and King (106) divided a soil sample into six mechanical fractions (average diameter 0·06, 0·034, 0·016, 0·006, 0·003, and $<$ 0·003 mm.) and found that on a weight basis phosphate retention increased with decreasing particle size, though on a surface-area basis the reverse held. The phosphate was added as monocalcium phosphate. Owen (104) found a fairly close relationship between phosphate retention and clay percentage that could be described by the regression equation

$$\log y = a + b \log m,$$

where y = percentage retention, m = percentage clay, and a and b are constants. Other workers have found a similar relationship (7, 103).

Coleman (20) found that the fine ($< 0{\cdot}2\mu$) kaolinitic and montmorillonitic clay fractions of two soils sorbed over twice as much phosphate per gm. of clay as the corresponding coarse (2–0·2μ) fractions. Using the minerals quartz, hematite, muscovite, phlogophite, biotite, pyrophyllite, talc, montmorillonite, and kaolinite, Perkins and King (108) showed that the retention of phosphate increased with their fineness of grinding.

The effect of the chemical composition of the colloid fractions of soil is discussed later.

2. *Phosphate concentration*

Russell and Prescott (123), Hibbard (59), Davis (27), Kurtz, DeTurk, and Bray (67), and Owen (104) have shown that the greater the ratio of phosphate to soil, the greater is the retention of phosphate. Laatsch (68) found that this also applies to NH_4^+ permutite. The relationship between phosphate retention and phosphate concentration has been shown to comply with the Freundlich adsorption isotherm (27, 67, 104, 123). Fisher (42) has pointed out that this does not necessarily imply an adsorption process, as precipitation processes also give results which fit the Freundlich adsorption isotherm.

3. *Time and temperature*

Retention of phosphate differs from the retention of cations in that the reaction comes to completion only very slowly, if at all. It has been shown that with soil and with soil clay the initial stages of the reaction proceed rapidly, but the reaction, although getting slower, continues for many weeks (19, 27, 59, 67). A similar effect of time has been observed with kaolinite by Black (10), and with muscovite, montmorillonite, hematite, and limonite by Perkins (110). Black (10), Coleman (19),

and Perkins (110) have shown that the amount of phosphate sorbed by the clay minerals increases much more with time at pH 3–4 than at pH 6–7.

Scarseth and Tidmore (124), on the other hand, reported practically no difference in the amount of phosphate 'fixed' after 1 hour and after 20 days. They used 0·05 normal and 0·1 normal sulphuric acid to measure 'fixation'.

The solubility in dilute acids of phosphate that has been added to soil has been shown to decrease with time. This has been demonstrated with 1 and 2 per cent. acetic acid and CO_2-saturated water (4), with 0·002 normal sulphuric acid (59, 97, 125), with 0·01 normal sulphuric acid (104), and with dilute acetic acid (50). Williams and Stewart (159) found a very rapid decrease in solubility in calcium lactate, magnesium bicarbonate, acetic acid, potassium bisulphate, citric acid, and sodium hydroxide solutions.

Under sterile conditions phosphate retention increases only slightly as the temperature is increased from 25° C. to 35° C. (158). If the temperature is increased up to 100° C. the reaction proceeds much more rapidly (7, 57), though there is no evidence that the total amount of phosphate that can be retained is increased. If clay or soil is heated to much higher temperatures the hydrous minerals lose water and hydroxyl groups and their capacity to retain phosphate is decreased, though this does not apply to the hydrous aluminium oxides (44, 66). The effect of temperature on the retention of phosphate under non-sterile conditions would be expected to depend on the relative rates of mineralization of soil organic matter, thus allowing release of phosphate, and on the absorption of phosphate by micro-organisms. Consideration of these factors is, however, outside the scope of the present review.

4. *Effect of salts*

According to Liebig (72) sodium chloride, sodium nitrate, and ammonium salts increase the water solubility of calcium phosphate. Liebig argued that this increased solubility would still be exerted in the presence of soil and hence these salts would increase the diffusion of phosphatic fertilizers through the soil. Dyer (39) carried out analyses of the soil from the continuous-wheat plots at Rothamsted and found that the salts potassium, sodium, and magnesium sulphates had permitted greater penetration of the phosphate that had been applied as superphosphate. The phosphate that was retained was more easily soluble in 1 per cent. citric acid than on the plots not receiving these salts.

McGeorge and Breazeale (75) found that all the neutral salts that they tried decreased the solubility of rock phosphate and soil phosphate. Greaves (54) found that potassium chloride, sodium chloride, calcium chloride, calcium nitrate, and calcium sulphate decreased the solubility of the phosphate of these two materials, but sodium nitrate, potassium sulphate, and ammonium sulphate increased the solubility. Midgley (94) reported that potassium sulphate and ammonium sulphate slightly decreased, and calcium hydroxide considerably decreased the penetration of superphosphate through a slightly acid silt loam, whereas the penetration was considerably greater in the presence of sodium nitrate.

On the other hand, Brown (12) showed that sodium nitrate or ammonium sulphate when added to a slightly acid subsoil in a laboratory percolation experiment resulted in practically no increase in the penetration of phosphate that could be detected by the method of Truog and Meyer (144). Also, Hibbard (59) found that calcium sulphate and calcium and magnesium carbonates considerably depressed the water solubility of the phosphate that had been applied to four soils, but sodium sulphate and ammonium sulphate had practically no effect and potassium and magnesium sulphates had only a slight depressive action.

Eriksson (40, 41), working with acidic Swedish soils, showed that the solubility and availability of phosphate are considerably lowered by the presence of potassium chloride. The effect increased with an increase in the salt concentration. A similar effect on phosphate solubility has been reported by Kurtz *et al.* (67).

There is, as yet, insufficient knowledge to explain these apparently contradictory results. In soils in which calcium phosphate is formed, the addition of a calcium salt which involves no change in pH would be expected to decrease phosphate solubility by the common ion effect, and other neutral salts would be expected to increase the solubility by lowering the activities of the phosphate and calcium ions. This latter effect is well known in analytical chemistry.

Cameron and Hurst (14) found that neutral salts depressed the solubility of aluminium phosphate. Similar observations were made by Karlsson and Mattson (65) with an aluminium phosphate precipitate at pH values above its iso-electric point (pH 5). At lower pH values the effect was reversed. This might explain the observations that have been made by Eriksson (40, 41) and by Kurtz and his co-workers (67).

Cameron and Hurst (14) reported that the solubility of ferric phosphate was decreased by potassium chloride and sodium nitrate, but slightly increased by potassium sulphate.

B. *The Nature of the Retained Phosphate*

1. *Iron and aluminium compounds*

Voelcker (147), in 1863, showed that a sample of clay soil containing only a small percentage of calcium carbonate was active in phosphate sorption. He concluded that this was due to the formation of insoluble compounds with the hydrous iron and aluminium oxides that were known to be present, and to the consequent precipitation of calcium phosphate. A few years later Warington (151) found that artificially prepared hydrous ferric oxide and alumina retained considerable amounts of phosphate from solution, even in the presence of carbon dioxide. He determined (152) the retention of phosphate by two soils which had been treated with dilute acetic acid to remove calcium, and found that the soil with the greater amount of iron and aluminium soluble in hydrochloric acid retained the greater amount of phosphate. He thought that 'in all soils containing a sufficient amount of oxide of iron or alumina, the phosphoric acid will be found in combination with these bases, and not as alkaline or alkaline-earthy phosphate'.

As it became known that the water-solubility of the phosphate in superphosphate was reduced by the presence of iron and aluminium compounds, so was it inferred that in soils also, which were known to contain these compounds, phosphate reacted to form insoluble iron and aluminium phosphates. Thus, Dehérain (30) thought that iron and aluminium phosphates were gradually formed in the unmanured experimental plots at Grignon. In 10 years there was a loss of 800 kilograms per hectare of P_2O_5 which was soluble in dilute acetic acid. Gerlach (48) shook samples of a soil in 1 per cent. acetic acid for periods of 3 hours, 24 hours, and 14 days and found that 0·0103, 0·0079, and 0·0024 gm. P_2O_5 was dissolved. He attributed this diminution in the amount of phosphate extracted to a gradual sorption of the phosphate by iron or aluminium hydroxide after it had been dissolved from the more soluble phosphates. Similar observations were made by Russell and Prescott (123) in more exhaustive work.

In the last 30 years an intensive study has been made of the reactions that take place between soil and phosphate ions, and much of this work has been directed to elucidating the part played by iron and aluminium. These elements are found, in most soils at least, concentrated in the clay fraction. They both occur in the clay minerals themselves in octahedral linkage, and aluminium is found also in tetrahedral linkage. They can both occur as free hydroxides and oxides, aluminium as gibbsite [$Al(OH)_3$] (1), and iron as hematite [Fe_2O_3], goethite and limonite [$FeO(OH)$] (100), and as magnetite [Fe_3O_4] (15). Except in acid soils the amount of each in the soil solution is small. Magistad (82) found that the concentration of aluminium in soil solutions is only likely to be greater than 3 p.p.m. outside the pH range 4·5–8·0. Aluminium ions are considered by some workers to be present as exchangeable cations as it is known that aluminium comes into solution when an acid soil is leached with a neutral salt (105). Iron is present in soil organic matter (149), and aluminium probably occurs similarly.

It is now established that iron and aluminium hydrous oxides can sorb phosphate under the conditions that normally exist in soils. This has been demonstrated with hydrogels (51, 70, 76, 96, 98), with ferric hydroxide (66), and with soluble iron and aluminium (46, 84, 98, 114, 139, 141). Ford (44) showed that goethite and bauxite, but not hematite, retained phosphate from solution, and the phosphate retained by goethite had a very low solubility in 0·002 normal sulphuric acid. Perkins and King (109) found that limonite and one sample of hematite sorbed about 1 per cent. of their own weight of phosphoric acid, but another sample of hematite and magnetite sorbed practically no phosphate. Weiser (157) also reported that hematite sorbed no phosphate and thus differed from the hydrous oxides of iron such as limonite and goethite.

Thus, on *a priori* grounds the formation of iron and aluminium phosphate in soil would be expected. Support for this conclusion comes from four types of evidence.

(*a*) Correlations have been established between phosphate sorption and the amounts of iron and aluminium in soils.

Phosphate sorption has been shown to vary inversely as the SiO_2/

($Fe_2O_3+Al_2O_3$) ratio of soil colloids (83, 87, 124, 142). Gaarder and Grahl-Nielsen (47) showed that the phosphate sorption capacity of forty three soils increased with the ratio of basoids to acidoids. Gile (52) found in a pot experiment that the efficiency of superphosphate decreased as the $SiO_2/(Fe_2O_3+Al_2O_3)$ ratio of the soil colloids decreased.

The amount of iron and aluminium which is soluble in acids and the amount of phosphate that the soils sorbed have been correlated (3, 45, 118).

A correlation between the amounts of iron and aluminium and phosphate dissolved by dilute acids has also been established (19, 104, 148).

Metzger (93), using forty two soil samples, found a significant correlation between total Al_2O_3, Fe_2O_3, ($Al_2O_3+Fe_2O_3$), and phosphate sorption. He also found that the reduction in phosphate sorption capacity, due to extraction with 0·002 normal sulphuric acid, when expressed as a percentage of the original sorption capacity was correlated with the amount of iron that was soluble in the extracting reagent. He established a correlation between the percentage of total Fe_2O_3 that dissolved in 0·002 normal sulphuric acid and the percentage reduction in the phosphate sorption capacity that resulted from acid extraction. A similar correlation was not found with aluminium.

(*b*) Iron and aluminium have been removed from soils and soil colloids and the effect on phosphate sorption has been studied.

Toth (142, 143) and Kelly and Midgley (66) used the hydrogen sulphide method of Drosdoff and Truog (38) to show that the removal of iron and aluminium oxides from soil colloids reduced phosphate sorption. The effect varied with the colloid under investigation. A similar result has been reported by a number of workers (10, 17, 18, 20, 92) after the iron and aluminium had been removed by a slightly modified hydrogen sulphide method (145). However, it has never been proved that the clay minerals remain unaffected by the reagents used to extract iron and aluminium oxides and, in fact, Toth (143) and Dion (33) have reported evidence of such decomposition. Romine and Metzger (121) showed that the phosphate sorption capacity of soil was lower after extraction with 0·002 normal H_2SO_4.

Ghani (49) found that the addition of 8-hydroxyquinoline to soil reduced the sorption of phosphate under acid conditions. As 8-hydroxyquinoline was thought to block active iron and aluminium, this was taken as evidence for the formation of iron and aluminium phosphates.

(*c*) Iron and aluminium compounds have been added to soils and soil colloids and the effect on phosphate sorption has been studied.

Wolkoff (161) found that the addition of ferric chloride to a soil treated with rock phosphate reduced the amount of phosphate dissolved by 0·2 normal nitric acid. Aluminium chloride had no effect. Doughty (36) saturated a peat soil with iron and aluminium ions by leaching with solutions of ferric chloride and aluminium chloride. He found that both the iron and aluminium caused a considerable increase in phosphate sorption. The maximum sorption was at pH 2·5 following the ferric chloride treatment, and at pH 4·0 after leaching with aluminium chloride. Scarseth (126) found that a low-iron bentonite sorbed much more

phosphate in the pH range 3·0–7·0 after being treated with a ferric chloride solution.

Davis (25, 26) reported that ferric chloride and aluminium chloride that had been added to soil-$Ca(OH)_2$-H_2O-air systems increased phosphate sorption especially at low pH values. In the sample treated with ferric chloride retention against 0·002 normal sulphuric acid and 0·1 normal sulphuric acid was also increased. He concluded that only at pH values lower than 4·5 are appreciable amounts of iron and aluminium phosphates formed that are insoluble in 0·002 normal sulphuric acid.

(*d*) Compounds formed during phosphate sorption have been identified by comparing the effect of pH on phosphate sorption with the known effect of pH on the solubility of iron and aluminium phosphates.

The effect of pH on the precipitation of iron and aluminium phosphates has been studied by Teakle (141). With iron, precipitation of phosphate was greatest at pH 3·0, and with aluminium, at pH 6·8.

With equivalent amounts of $Fe^{\cdots}$ and PO_4''', Doughty (36) found that the greatest precipitation was at pH 3·5–4·5 and Gaarder (46) at pH 2·0–3·0. Both workers reported that precipitation takes place up to at least pH 8 in the presence of a considerable excess of iron. With equivalent amounts of $Al^{\cdots}$ and PO_4''', Doughty found greatest phosphate precipitation at pH 6·8, and Gaarder at pH 3·6–4·0, but with an excess of aluminium Doughty found the pH range of greatest precipitation became 6·5–8·5, and Gaarder 4·5–6·5. Rathje (116) found that the greatest precipitation of phosphate by excess iron was at pH 3, and at pH 4 with excess aluminium.

Results from similar experiments have been obtained by Murphy (98) using ferric chloride and an iron hydrosol, and by Perkins and King (109) with limonite and hematite. McGeorge and Breazeale (76) and Stelly and Pierre (135) have reported results on the effect of pH on the solubility of iron and aluminium phosphate minerals. Stelly and Pierre found that the lowest solubility of the aluminium phosphate minerals wavellite and variscite was in the pH range 4·5–7·0, and of the iron phosphate minerals vivianite and dufrenite was in the pH ranges 6·0–7·0 and 3·0–6·0 respectively.

The first experiment to be reported that accurately related phosphate sorption of soil to the pH value was that of Roszmann (122). He found that the greatest sorption with the electrodialysed clay fraction of Putnam silt loam was at pH 3·0–4·0, with little sorption above pH 10.

Doughty (36) studied the retention of phosphate by a peat soil over the pH range 3–10 and attributed the retention at low pH values to iron and aluminium. Scarseth (126) found that the greatest retention of phosphate by an electrodialysed bentonite titrated with sodium hydroxide was at pH 6–7, which he thought was due to a reaction of the phosphate with the aluminium of the clay mineral. Allison (2) found a similar maximum at pH 6 with three soil colloids titrated with sodium hydroxide. He found another peak in the phosphate sorption-pH curve at pH 3·0–3·5 which he attributed to the presence of iron and aluminium hydrous oxides, especially the former.

Black (10) working with Cecil Clay, found a maximum in the phos-

phate-sorption curve at pH 3–4, which he thought was due to hydrous iron oxide. He found that the amount of phosphate that was sorbed at this maximum was reduced by the removal of the free iron oxide, but it still remained appreciable. He also concluded that the maximum in the phosphate-sorption curve at pH 6–7, which he found with a sample of 2μ kaolinite, was due to adsorption by free aluminium hydroxide. The aluminium was thought to come slowly into solution, especially under more acid conditions, because after 30 days' shaking the maximum had shifted to pH 5–6.

Coleman (18, 20) using montmorillonitic and kaolinitic clays showed that most sorption of phosphate took place at pH 3·0, but after removal of free iron oxides the sorption was reduced so as to be about the same at pH 3·0, 7·0, and 9·5.

Mechanism of the reaction with iron and aluminium. Reference has already been made to the work of Russell and Prescott (123). These workers found that if soils were extracted with acids of low concentration (N/20 to N/10) the amount of phosphate that was extracted decreased with an increase in the time of the extraction. The action of dilute acids thus seemed to consist of two parts:

1. A direct solvent action of the acid on the phosphorus compounds of the soil that depended only on the concentration of the acid, and not on its nature.
2. A retention of the liberated phosphate that was greatest in the presence of mineral acids such as nitric and hydrochloric acids and least in the presence of organic acids such as citric and oxalic acids.

They argued that the retention of phosphate was more likely to be due to adsorption than to precipitation as the reaction was found to follow the Freundlich adsorption isotherm. Also, they found that there was no precipitation of phosphate by a soil extract that would have contained any soluble compounds capable of precipitating the phosphate, and they also assumed that the concentration of acid they employed would prevent the precipitation of insoluble phosphates. Their argument has been criticized by Fisher (42) and Comber (21). Fisher pointed out that compliance with the Freundlich equation is not restricted to adsorption reactions, whilst Comber showed that the strengths of acid used by Russell and Prescott were not sufficient to prevent the precipitation of phosphate. Murphy (98) objected to the precipitation theory on the grounds that only under conditions of extreme acidity is sufficient iron or aluminium present in the soil solution to cause rapid precipitation, though for this criticism to be valid it would be necessary to show that the soil solution cannot be rapidly renewed by dissolution of iron or aluminium from the solid phase.

It has already been pointed out that numerous workers have shown that iron and aluminium hydroxides and hydrous oxides can sorb phosphate. It has therefore been postulated that there is an exchange reaction between phosphate ions (mainly H_2PO_4' and HPO_4'') and the hydroxyl ions present in these compounds (56, 86, 87, 115). Kelly and Midgley

(66) found an increase in pH value when ferric hydroxide and a phosphate solution at the same pH value were mixed. Ford (44) and Kelly and Midgley (66) showed that only iron oxide that is hydrated will retain phosphate and the substance loses this property if it is strongly heated. Heck (56) believed that in Hawaiian soils, which are known to fix phosphate very strongly, a basic ferric phosphate is formed, i.e. not all the hydroxyl groups are replaced. Swenson, Cole, and Sieling (139) have claimed that not more than one of the hydroxyl ions of iron and aluminium hydroxides can be replaced.

Mattson and Karlsson (89) and Karlsson and Mattson (65) studied the effect of salts on the retention of phosphate by aluminium hydroxide and concluded that phosphate ions may be 'saloid-bound' or 'colloid-bound', that is, be 'gegen-ionen', or be chemo-sorbed. The phosphate is predominantly 'saloid-bound' when the precipitate has a positive charge, as it has at low pH values. Both Mattson (83) and Schofield (130) attributed the retention of chloride and sulphate ions by clay at low pH values to the presence of free hydrous iron and aluminium oxides, especially the former.

Although there is good evidence that either iron or aluminium, or both, can react with phosphate under the conditions that exist in soil, it cannot be stated with certainty whether these ions come from the clay minerals or from the free hydrous oxides. There seems no reason why they should not come from both. Further, there is uncertainty on the mechanism of the reaction. The distinction between precipitation on the one hand, and adsorption with the formation of chemical bonds (chemo-sorption) on the other, is a fine one, and will be difficult to resolve.

2. *Calcium and magnesium compounds*

Both Way (154) and Voelcker (147) supposed that an insoluble calcium phosphate is formed when a soluble phosphate is mixed with soil containing calcium carbonate. This insoluble phosphate was assumed to be either dicalcium phosphate or tricalcium phosphate (48, 62, 129, 137), though tricalcium phosphate was thought to be produced in all soils containing more than a trace of calcium carbonate. Bassett (6), however, after a phase-rule study of the system CaO-P_2O_5-H_2O concluded that a more basic compound such as hydroxy-apatite would be formed in neutral and calcareous soils. McGeorge and Breazeale (75) later postulated the formation of carbonate-apatite in soils containing a high percentage of calcium carbonate.

Dean (28) fractionated the phosphorus contained in the slightly calcareous soil at Rothamsted and concluded that the phosphorus which had been applied as superphosphate had been retained as tricalcium phosphate or apatite. Direct evidence for the formation of a fluorine-containing apatite on this soil was later obtained by Nagelschmidt and Nixon (101) from examination of the chalk fragments by an X-ray diffraction technique and chemical analysis. This confirmed an earlier suggestion by MacIntire and Hatcher (80) that fluorapatite is formed in calcareous soils.

There is also evidence that phosphate ions can be retained through exchangeable calcium. Naftel (99) thought that this type of adsorption could take place up to about pH 6·5, but that at higher pH values tricalcium phosphate or apatite is precipitated. Other workers have postulated that exchangeable calcium can retain phosphate at pH values as low as 4·0 (2, 5, 126) or below (111). Phosphate is not precipitated from solution by Ca^{++} ions at pH values lower than about 5·0 (9, 46). Boischot, Coppenet, and Hébert (11) have recently put forward the suggestion that in calcareous soils the initial reaction is an adsorption on to the surface of calcium carbonate particles rather than to precipitation of an insoluble phosphate.

Perkins (111) found that up to pH 4·5, Mg^{++} ions that had been added to 100-mesh kaolin were about as effective as an equivalent amount of Ca^{++} ions in precipitating phosphate, but at higher pH values they were far less effective. He concluded that precipitation of phosphate by magnesium is not likely to be of importance in ordinary agricultural soils.

Not only is the final product important, but it is also important to know the rate at which the various forms of calcium phosphate are formed. MacIntire and his co-workers (77, 78, 79) showed that dicalcium phosphate when mixed with calcium carbonate and distilled water and kept under laboratory conditions undergoes only slow transformation to tricalcium phosphate. Thirty per cent. of the dicalcium phosphate was converted to the triphosphate in the first week, but after 12 months 40 per cent. of the dicalcium phosphate remained unchanged. They suggested (80) that the dicalcium phosphate probably persists in moderately limed soils for a considerable period. In most calcareous soils the calcium carbonate : calcium phosphate ratio is much wider than they employed and the rate of transformation might therefore be expected to be more rapid.

The size of the apatite particles that are formed is not known, but MacIntire and Hatcher (80) suggest that compared with finely ground rock phosphate they are of 'infinitesimal fineness'. This fineness of division is one of the factors that determines the availability of the apatite to plants.

3. *Compounds with clay minerals*

Montmorillonite. Scarseth (126) working with a low-iron bentonite that had been electrodialysed found that the greatest sorption of phosphate by the Na-clay was at about pH 6·5. He thought that there was an exchange between PO_4''' and $3OH'$ groups which dissociated from aluminium ions present at the surface of the alumino-silicate. Murphy (98) found that bentonite sorbed only half as much phosphate as did kaolinite, but he did not report the relative fineness of the two minerals. Similarly, Stout (138) reported a sorption at pH 7 of 11 milli-equivalents of phosphate per 100 gm. bentonite, whereas with ball-milled kaolinite under similar conditions 172 milli-equivalents of phosphate were sorbed. Maximum sorption with the bentonite occurred at pH 6.

Differing from this work is that of Black (10), Coleman (18, 19), Perkins and King (108), and Perkins (110), who have shown that sorp-

tion of phosphate by montmorillonite can be at least as great as by kaolinite if minerals of similar fineness of grinding are used. Black (10) found the greatest retention by bentonite ($< 2\mu$) at pH 5–6.

Kaolinite. Both Murphy (98) and Stout (138) studied phosphate sorption by the mineral kaolinite after it had been ball-milled. They found that sorption was high and that it increased as the pH value decreased to 3·0, the lowest value investigated. Black (10) showed that ball-milled kaolinite sorbed many times more phosphate than coarse ($< 2\mu$) kaolinite, but thought that the difference was due to the kaolinite crystals having been 'split and disorganized' during ball-milling. He found one maximum in the pH-phosphate sorption curve at pH 3·5–4·0 which he attributed to the replacement of the hydroxyl ions of the lattice layers of the kaolinite. With the coarse kaolinite there was another maximum at pH 6–7 which he thought was due to the formation of aluminium phosphate on the surface of hydrous aluminium oxides.

Cooke (22), Midgley (95), and Raychaudhuri and Mukherjee (118) reported that unground kaolinite sorbs little phosphate. On the other hand, Perkins (112), using kaolinite that had been ground to pass a 100-mesh sieve, found that almost 40 per cent. of the phosphate that had been supplied at the rate of 0·355 gm. H_3PO_4 per 100 gm. clay was retained in a few hours' shaking.

It is doubtful whether the experiments using ball-milled kaolinite give results at all analogous with those of soil clay because there is evidence that prolonged ball-milling induces changes in the crystalline structure of kaolinite. Sieling (133) found that the constituent of ball-milled kaolinite that was active in phosphate sorption could be extracted by 0·1 normal hydrochloric acid or 0·1 molar tartaric acid and believed it to be a form of hydrous alumina such as γ-AlOOH. Laws and Page (69) adduced evidence for the formation of a new permutite-like mineral when kaolinite is ball-milled for a long period. Perkins (112) has also given evidence that grinding causes a disruption of the kaolinite lattice that was manifested by a release of Al_2O_3, SiO_2, and water.

Stout (138) and Black (10) have reported that halloysite, which has a crystalline structure similar to that of kaolinite, can sorb a large amount of phosphate. Stout showed that halloysite sorbed slightly more phosphate than kaolinite over the pH range 3–10 and found greatest phosphate sorption by both minerals at pH 3, the values being 1,290 and 1,170 m.e. phosphate per 100 gm. mineral respectively. Each mineral had been ball-milled. Black (10) reported that the maximum sorption by 60-mesh halloysite was at pH 4–5 from a solution of 1 p.p.m. phosphorus, and at pH 3·1 from a solution of 100 p.p.m. phosphorus.

Mica. Black (10) reported that a sample of illite which contained free iron oxides sorbed up to 10 per cent. of the phosphate in 48 hours from a solution of 100 p.p.m. phosphorus. The maximum from a solution of 1 p.p.m. phosphorus was at pH 5–6, and from a solution of 100 p.p.m. phosphorus at pH 3.

Perkins and King (107, 108) found that the micas muscovite, biotite, and margarite sorb large amounts of phosphate, which they attributed to the replacement of lattice silicon by aluminium.

There seems to have been no study made of the phosphate-retaining properties of the hydrous micas.

Mechanism of the reaction with clay minerals. There are two types of reaction by which phosphate ions might be retained by the clay minerals: by the formation of chemical bonds with lattice ions, and by adsorption as gegen ions.

Iron and aluminium are the only lattice ions that are likely to undergo a reaction with phosphate ions. The phosphate ions may be retained by an exchange reaction with the hydroxyl ions that are normally linked with the iron and aluminium ions. Alternatively, the iron and aluminium may acquire a positive charge by the transfer of a proton from an H_3O^+ ion to an oxygen, as has been suggested by Schofield (130) for hydrous iron oxide. The former suggestion has been made by a number of workers (10, 29, 86, 115, 117, 126, 138, 142). The most direct evidence to support this postulate was presented by Stout (138). He showed that after being phosphated, the minerals kaolinite and halloysite contained fewer hydroxyl ions, for they lost less water on heating. It must, however, be borne in mind that Stout used ball-milled minerals which might have contained degradation products (*v. supra*).

Perkins and King (107) compared the retention of phosphate by the minerals pyrophyllite [$Si_4O_{10}Al_2(OH)_2$] and talc [$Si_4O_{10}Mg_3(OH)_2$], muscovite [$KAlSi_3O_{10}Al_2(OH)_2$] and phlogophite [$KAlSi_3O_{10}Mg_3(OH)_2$]. They claimed that the pH values at which they found greatest precipitation were those that would be expected by a reaction of the metal to which the hydroxyl ions were attached. This is not clearly revealed by their published results. Thus there is some evidence, though not conclusive, that phosphate ions can replace the hydroxyl ions which are attached to the lattice ions of the clay minerals.

A different theory has been put forward by Low and Black (74). They showed that the addition of increasing amounts of phosphate to a sample of kaolinite at pH 4·5–4·7 brought increasing amounts of silica into solution. They took this as evidence for the disintegration of the surface layers of the kaolinite with the formation of insoluble aluminium phosphate and the release of silica. According to Mattson (87, 88) and Toth (142), silicate ions from artificial aluminium silicate and from some clays can be replaced by phosphate ions.

It is well established that the phosphate ions which are retained by clay particles can be replaced by other anions, at least partially. The order of replacing power of other anions depends not so much on their valency, as might be expected from the Hardy-Schulze valency rule, as on their chemical nature. Thus, it has been shown that citrate, tartrate, oxalate, arsenate, and fluoride have strong replacing properties whereas sulphate, thiocyanate, acetate, chloride, and nitrate have only weak replacing properties (29, 31, 32, 67, 123, 131). Swenson and his co-workers (139) have pointed out that the anions which are most effective in replacing phosphate can themselves form complexes with iron and aluminium.

There is no satisfactory evidence that the clay minerals have amphoteric properties and can therefore adsorb phosphate ions as gegen ions.

Mattson (83) showed that if clay particles have a low $SiO_2/(Fe_2O_3+Al_2O_3)$ ratio they become positively charged at low pH values. The retention of chloride and sulphate ions increased as the positive charge increased, though there was a small retention of both ions when the particles had a small negative charge. Schofield (130) has also shown that at low pH values chloride ions can be retained by clay particles even though they have a net negative charge. Both these workers have attributed this manifestation of the amphoteric properties of the clay to the free iron oxide and not to the clay minerals.

The replacement of a small amount of the adsorbed phosphate by chloride ions has been attributed to a replacement of gegen ions (159). This phosphate is termed 'saloid-bound' according to the terminology of Mattson and Karlsson (89). There is, however, no evidence to decide whether the clay minerals or the free hydrous iron and aluminium oxides are responsible for this type of adsorption.

4. *Compounds with other inorganic soil constituents*

Quartz. It has been found that a silica hydrogel can retain some of the phosphate from a solution of monocalcium phosphate (51, 134). This was explained by Ghosh and Bhattacharyya (51) as being due to adsorption of phosphate through the calcium ions which are held by the silica gel. Perkins and King (109) and Perkins (110) showed that the retention of phosphate by finely ground quartz is very small, but in another experiment (108) they found that ball-milled quartz sorbed a considerable amount of phosphate. It is possible that this sample of quartz had been contaminated in the ball-mill.

Manganese. Teakle (141) reported that phosphate was least soluble in the presence of manganese chloride at about pH 6·3. He suggested that $Mn_3(PO_4)_2$ might form in soil at this and slightly lower pH values.

Titanium. According to Pugh (114) titanium chloride can precipitate phosphate at low pH values, but the precipitate hydrolyses at pH values above about 6. Perkins and King (109) found that 100-mesh rutile sorbed up to 0·29 gm. H_3PO_4 per 100 gm. The greatest sorption was in the pH range 3·5–5·0.

5. *Compounds with organic matter*

The retention of phosphate by the non-living organic matter in soil is usually believed to be small (13, 113). Doughty gave evidence that such retention as there is is due to a reaction of the phosphate with Fe^{+++}, Al^{+++}, and Ca^{++} ions which are associated with the organic matter (36, 37). Chaminade reported that humus forms a complex with phosphate ions which is not readily precipitated by Ca^{++} ions, even at high pH values (16). Other workers have shown that the humate ion can replace the phosphate ions that are adsorbed by clay minerals and by artificial alumino-silicates (85).

The part played by soil micro-organisms in retaining phosphate has never been thoroughly investigated. Lockett (73) has referred to some of the early literature. Pierre, in 1948, in a valuable review, suggested that micro-organisms may immobilize a large amount of phosphate

when a source of nitrogen and energy is available (113). A year earlier Taylor (140) had published the results of some preliminary experiments which led him to the same conclusion. He found that the sorption of phosphate by a garden soil was substantially increased by the addition of peptone, urea, and blood meal. Sterilization of the soil by heat and by certain chemicals prevented this increase, but did not reduce the amount of phosphate retained when no organic supplements had been given. The author therefore concluded that inorganic phosphate is unlikely to be metabolized by micro-organisms unless phosphate is their limiting growth factor in the soil. At the same time, addition of substances which stimulate the growth of micro-organisms leads to an absorption by the micro-organisms which may be appreciable. In Finland, Kaila has recently shown that the carbon/organic-phosphorus ratio in soils is roughly constant at 100–150, but if the ratio exceeds 200, inorganic phosphorus is liable to be biologically absorbed (63).

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THE INTERPRETATION OF X-RAY DIAGRAMS OF SOIL CLAYS

II. STRUCTURES WITH RANDOM INTERSTRATIFICATION

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In a paper which appeared in the last issue of this *Journal* (MacEwan, 1949), of which the present paper is to be considered a sequel, three ways were considered for the interpolation of sheets of water molecules between the layers* of a clay-mineral structure, and the corresponding X-ray diagrams considered. The second type of interpolation—the completely random type—was illustrated by curves, calculated from a formula developed by Hendricks and Teller (1942), showing the scattering to be expected from mixtures, in various proportions, of 10 Å and 15·4 Å layers and of 10 Å and 17·7 Å layers† (i.e. of mica and montmorillonite layers, hydrated and glycerol-saturated). These calculations have now been extended by Mr. Brown to cover a larger variety of cases and a larger range of reciprocal spacings, and the present paper consists essentially of the curves deduced and a brief commentary on them. While these calculations were in progress Mr. J. Méring sent us a copy of a paper to be published in *Acta Crystallographica* (1949) which develops Hendricks and Teller's theory so as to take account of the limited size of the crystallites. This paper, which is further mentioned below, confirms the general utility of the Hendricks and Teller formula, and it was not considered necessary, therefore, to amend the calculations in order to take account of the new work. Indeed this would have been difficult, for the new formula is so general that many more diagrams would have been necessary to present adequately all the cases with which it is capable of dealing. Méring's formula can be applied to the detailed interpretation of particular cases, of which adequate data are available: the calculations presented here will, it is hoped, be useful as a general guide to the interpretation of soil-clay diagrams.

Treatment of Hendricks and Teller

Hendricks and Teller (in the second section of their paper) have considered the case where a finite number r of phase changes can exist

* In this paper the term 'sheet' will be confined to a two-dimensional formation one molecule, ion, or atom thick, and 'layer' will be used for more complicated formations with two-dimensional regularity. This reverses the nomenclature which has been used in a previous paper by one of the present authors (MacEwan, 1948). The nomenclature used here has, however, been decided on by the Editor of *The Identification and Structural Relationships of Clay Minerals* (published by the Clay Minerals Group of the Mineralogical Society), and it seems desirable to conform to it.

† For the purposes of this paper it is not necessary to distinguish between the units Å and KX. The abbreviation Å is used throughout, and may be taken to represent either or both of them.

between layers and have worked out the scattering factor for the mixed structure on the following assumptions:

1. That all the layers have the same structure factor.
2. That the succession of the r phase changes is completely random, subject only to the probability factors f^1, f^2..., where

$$\sum_1^r f^s = 1.$$

3. That the crystallites are of infinite extent.

Of these three assumptions, the first and third are obviously impossible in practice. The assumption that all the layers have the same structure factor but different phase changes is equivalent to assuming that identical layers are separated by various distances, but with no material between them to support these varying separations. Any additional material, such as water molecules, which can cause variations in the interlayer distance will obviously also change the structure factor of the layer. In the case of water molecules, however, the scattering power is low compared with that of the layers themselves, so a formula based on assumption (1) will be expected to represent the actual scattering phenomena with tolerable accuracy. Where the interlamellar material is more dense, as in the mixed chlorite-vermiculite structures, the assumption becomes less accurate, though even in this case the curves reproduced here are likely to be of use as a general guide to the type of diffractions expected.

In section 3 of their paper Hendricks and Teller extend their treatment to cover the case where the layers have different structure factors. This treatment was not utilized, since the extra mathematical complication involved did not seem to be justified.

As regards the third assumption, it is the sort of limiting case which is commonly assumed in working out diffraction from crystals, and we may reasonably suppose that the actual finite size of the crystallites will lead to a broadening of the diffraction maxima without appreciable alteration in their position.

On these general grounds, it was considered that the Hendricks-Teller formula would represent the diffractions from mixed-layer clay minerals with adequate accuracy. The new treatment by J. Méring (1949) renders unnecessary the assumptions (1) and (3), enabling finite crystals and varying layer-structure factors to be considered. It confirms, in general, that with finite crystallites the same type of diffraction is obtained, but with a broadening of the diffraction maxima which is greater the smaller the number of unit layers in each crystallite. The treatment given in this paper, therefore, is likely to retain its utility, though it may be desirable to extend it at a later date in order to take account of the newer developments.

Formula for total scattering

Hendricks and Teller's formula gives only that portion of the total scattering function which is conditioned by the distribution of the layers. In order to get the total scattered intensity which is observed in

practice it must be multiplied by a factor F_l^2, representing the variation of scattered intensity due to the structure of the layers (which is, as already pointed out, assumed to be the same for all the layers), and by a factor Ξ which takes account of the polarization of the diffracted radiation and of the form of the specimen. The final formula which is derived for the scattered intensity given by a random mixture of two structures is as follows:

$$I = F_l^2 \Xi \frac{2f(1-f)\sin^2\pi\dfrac{d_2-d_1}{d'}}{1-2f(1-f)\sin^2\pi\dfrac{d_2-d_1}{d'}-f\cos 2\pi\dfrac{d_1}{d'}-(1-f)\cos 2\pi\dfrac{d_2}{d'}}. \quad (1)$$

Where:

f = proportion (expressed as a decimal fraction) of layers with higher spacing; and therefore $1-f$ = proportion of layers with lower spacing.

d' = 'apparent spacing' as measured on the film, i.e. it is $\lambda/(2\sin\theta)$, where θ = Bragg angle = $\frac{1}{4}(L/r)$; L = separation of corresponding points on either side of the centre of a cylindrical film (measured along the film), r = radius of camera. The reason for the use of the term 'apparent spacing' is that d', being continuously variable, does not necessarily represent any spacing which actually exists in the crystallites.

d_1 = higher inter-layer spacing.

d_2 = lower inter-layer spacing.

The factors F_l and Ξ are, of course, functions of the angle of diffraction and therefore of d'.

Form of function Ξ

The function Ξ can have the forms

$$\frac{2-\sin^2 2\theta}{\sin\theta\sin 2\theta} \quad \text{and} \quad \frac{2-\sin^2 2\theta}{\sin 2\theta}$$

respectively, depending on whether the specimen is of the powder type (unoriented) or a single crystal. Our curves are drawn mainly with the 'oriented aggregate' type of specimen in mind, since this is most likely to be used when studying basal reflections of clay minerals, and it is not possible to give any completely accurate formula which will be applicable to such a specimen. On the one hand, if the orientation is very poor, the resulting diffracted intensity will approach that given by a powder specimen; on the other hand, with very good orientation it will approach that for a single crystal. The main difference between the two formulae is that the powder specimen formula gives a more rapid rise of intensity as the centre of the photograph (i.e. the primary beam) is approached. The true rate of rise will be somewhere between the two; it will, however, be diminished appreciably by absorption in the specimen, which is not taken account of in the formulae quoted, and which, with an oriented aggregate specimen of normal size, and CuKα radiation, will lead to an intensity diminution in the ratio of about 1 : 2 near to the

primary beam (more if the specimen has a high iron content). We have therefore adopted the single crystal formula, as probably representing most nearly the true intensity distribution with a well-oriented specimen. In using the curves reproduced here it should therefore be remembered that with a powder specimen the intensity will go up more rapidly towards the centre: in fact, the intensity distribution for the powder specimen is obtained by multiplying the ordinates of our curves by the factor $1/\sin\theta = 2d'/\lambda \propto 1/s$.

One modification was made to the curves thus deduced in order to give a better representation of the true scattering phenomena. The formula quoted applies to infinite crystallites, and an indefinitely small specimen. Thus at certain points the scattering curve may reach very large or even infinite values. These, of course, are quite fictitious, and in practice the scattering at such points is always spread out due to the finite size of the crystallites and of the specimen. In order to give a better representation of what is actually seen on the photograph the final intensity function was therefore averaged over the range $\delta s = 0{\cdot}4$, i.e. in place of I given by formula (1), we have plotted the function

$$\left(\int_{s-\frac{1}{2}\delta s}^{s+\frac{1}{2}\delta s} I\,ds\right)\Big/\delta s.$$

Of course, it is only in the neighbourhood of a peak that this function is appreciably different from I.

This procedure does not allow for the finite size of the crystallites, a matter which has already been discussed: but it does give peaks of manageable size, and of the correct relative areas.

Description of curves

The curves give the total scattered intensity as a function of $s = 100/d'$, the reciprocal spacing, for values of s up to 33. For the region considered, s is very nearly proportional to distances as measured on the film, so that the curves can be compared directly with X-ray photographs.

The continuous line curves represent the intensity in arbitrary units, which, however, are the same for all the figures of one series (dioctahedral mica, trioctahedral mica, kaolin), the reflections of which may thus be compared between each other. The portions in dotted lines are on one-tenth of the intensity scale. The different curves of each set have been shifted vertically to avoid confusion, and the short lines on the left-hand margin indicate the base positions, corresponding to zero intensity. The top and bottom margins have an external scale of s-units, at intervals of 5. The internal scale gives the positions of the reflections of the two 'pure states' which contribute to the random mixtures, the non-hydrated one being on the top margin and the hydrated (or glycerolated) one on the bottom margin. The peaks are labelled according to the indices of the 'pure state' reflections with which they eventually merge; e.g. 003/004 in Fig. 1 is a peak which moves from the (003) position of the 10 Å material to the (004) position of the 12·4 Å material. Such a

symbol as −/002 in Fig. 3 indicates a peak which merges with (002) in the fully hydrated state, and disappears completely as the non-hydrated state is approached. In some cases peaks have been omitted if their position and magnitude can readily be deduced from the neighbouring peaks, and their insertion would cause confusion (two of the 003/004 peaks in Figs. 3 and 4).

Table 1 gives a list of the spacings and types of structure for which the curves have been calculated and an indication of the principal practical cases to which they could apply.

TABLE 1

Fig.	*Spacings* (Å) d_1	d_2	*Structural types*	*Practical cases*
1	12·4	10	Dioctahedral micaceous	Partly hydrated mica or montmorillonoid (one layer of water molecules).
2	12·4	10	Trioctahedral micaceous	
3	14	10	Dioctahedral micaceous	Interstratification of mica and vermiculite or chlorite (the latter only inaccurately, due to the different layer structure factors), partly hydrated Ca-montmorillonoid.
4	14	10	Trioctahedral micaceous	
5	15·4	10	Dioctahedral micaceous	Interstratification of mica and montmorillonoid (normally hydrated with two layers of water molecules).
6	15·4	10	Trioctahedral micaceous	
7	17·7	10	Dioctahedral micaceous	Interstratification of mica and glycerol-saturated montmorillonoid (two layers of glycerol molecules).
8	17·7	10	Trioctahedral micaceous	
9	10	7·15	Dioctahedral kaolin-type	Partly hydrated halloysite (applies approximately also to the same when glycerol-saturated).

In each case the values of f represented are 0·1, 0·2, 0·3, 0·5, and 0·7. The layer structure factors are calculated without taking account of the interamellar water molecules and potassium ions.

Inspection of these curves, Figs. 1–9, shows immediately that in each case well-defined sharp peaks are obtained with relatively little scattering between them. The presence of a random structure may, however, be deduced by means of two characteristics.

1. The peaks given by a random structure do not form an integral series, i.e. they do not occur at positions given by s_1, $2s_1$, $3s_1$.
2. The random structure gives a marked rise of scattering towards the centre of the photograph, i.e. near to the primary beam.

In view of the fact that individual peaks can always be picked out, the changes that take place in the X-ray diagrams as the proportions of the two types of layer are altered may be described in terms of movements of peaks. For this purpose the peaks in Figs. 1–9 have been

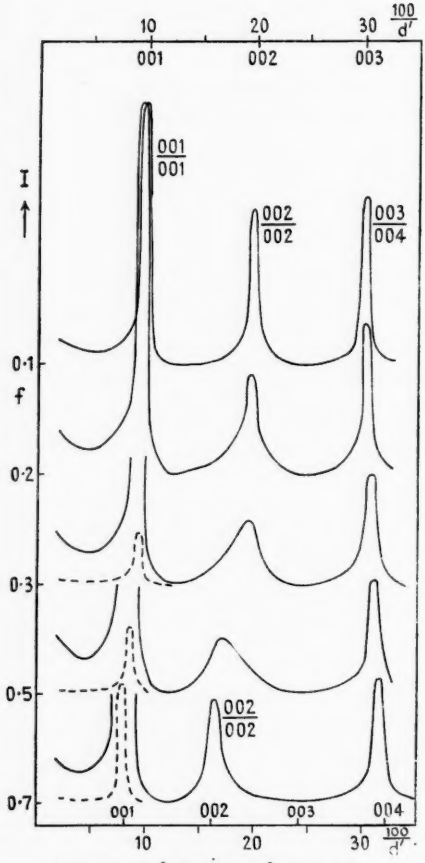

FIG. 1. 10 Å and 12·4 Å spacings: dioctahedral mica layers.

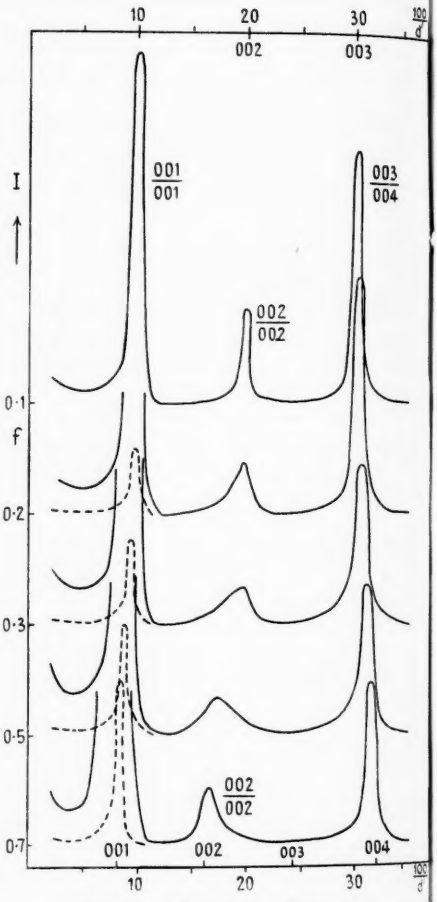

FIG. 2. 10 Å and 12·4 Å spacings: trioctahedral mica layers.

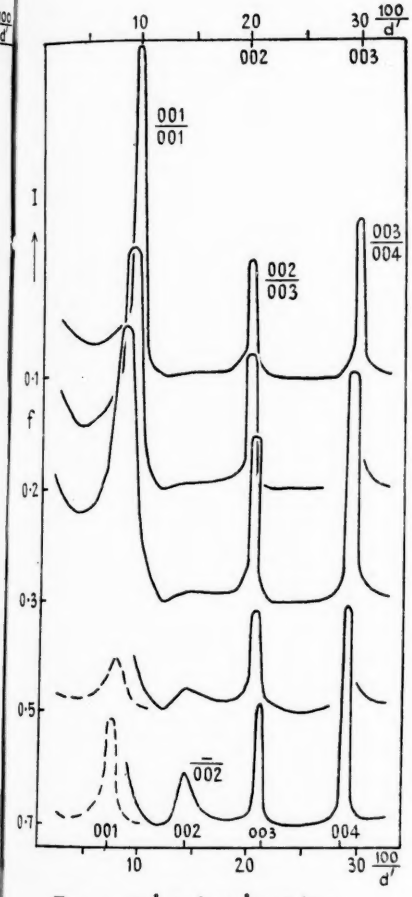

FIG. 3. 10 Å and 14 Å spacings: dioctahedral mica layers.

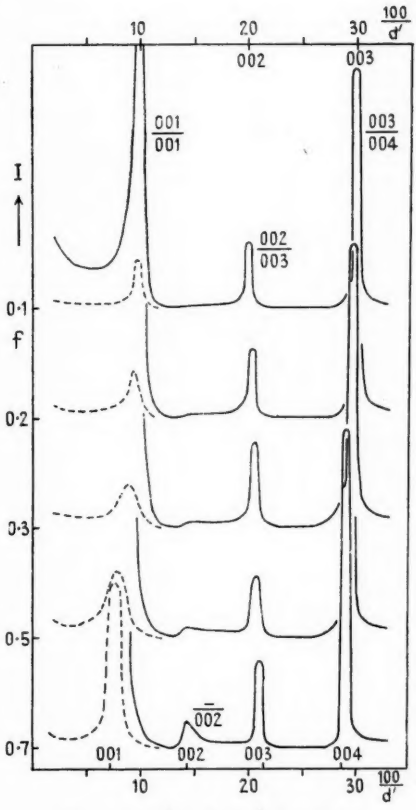

FIG. 4. 10 Å and 14 Å spacings: trioctahedral mica layers.

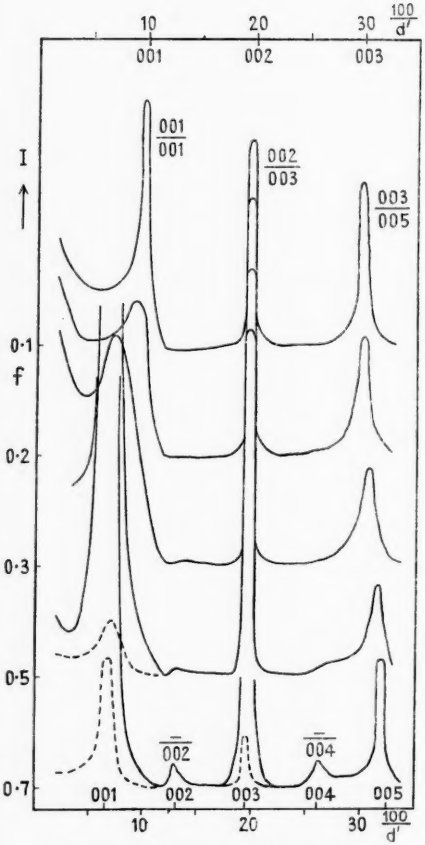

FIG. 5. 10 Å and 15·4 Å spacings: dioctahedral mica layers.

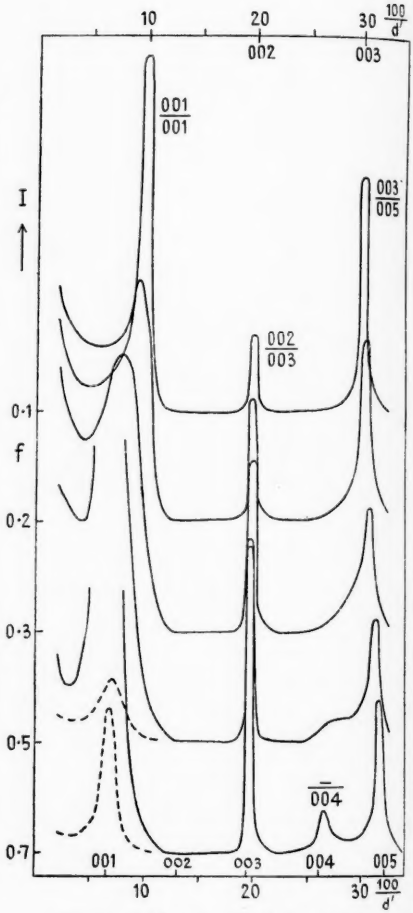

FIG. 6. 10 Å and 15·4 Å spacings: trioctahedral mica layers.

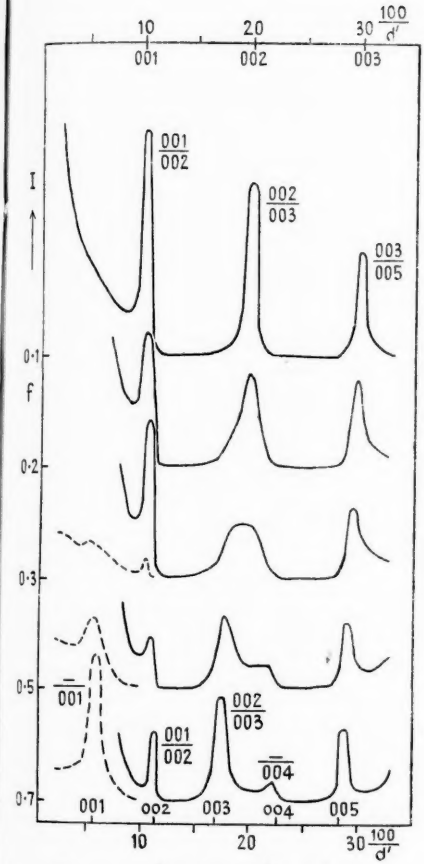

FIG. 7. 10 Å and 17·7 Å spacings: dioctahedral mica layers.

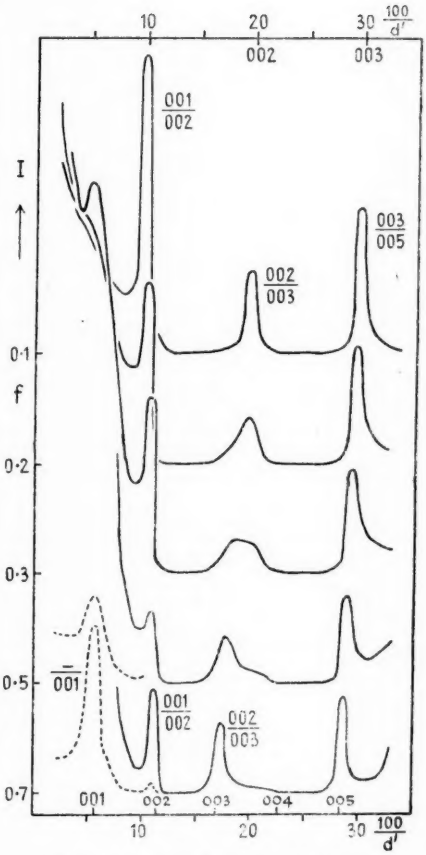

FIG. 8. 10 Å and 17·7 Å spacings: trioctahedral mica layers.

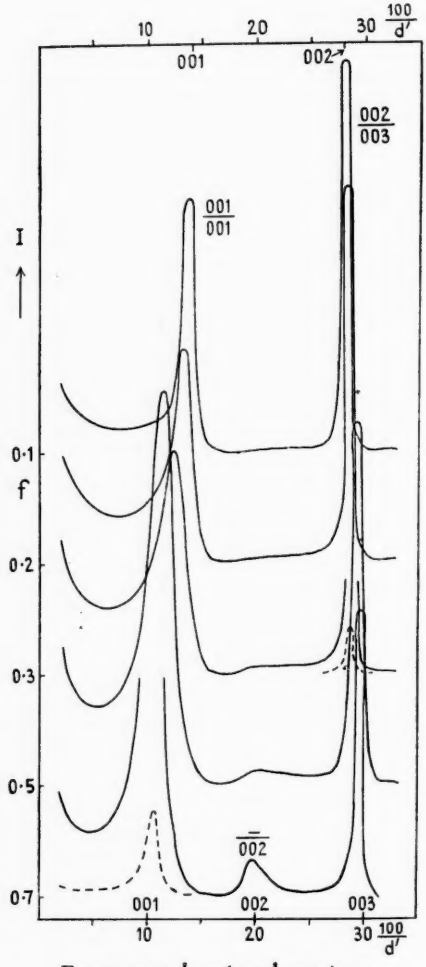

FIG. 9. 7·14 Å and 10 Å spacings: dioctahedral kaolin layers.

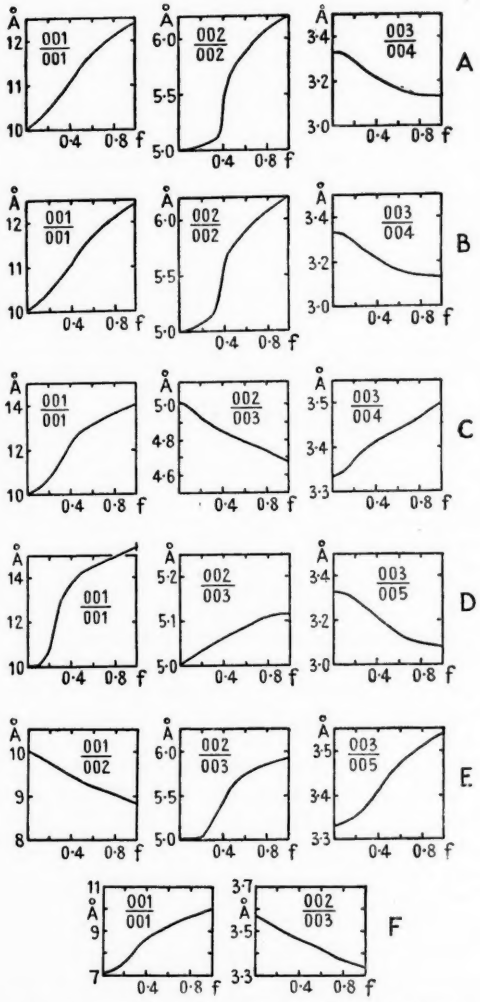

FIG. 10. Curves showing migration of peaks in figs. 1–9 A, 10/12·4 Å, dioctohedral. B, 10/12·4 Å, trioctahedral. C, 10/14 Å, di- and trioctahedral. D, 10/15·4 Å di- and trioctahehral. E, 10/17·7 Å, di- and trioctahedral. F, 7·14/10 Å, dioctahedral. (*Note.* There is a minor drawing error in the right-hand figures A and B. The curve at the point $f = 0$ should end at 3·10 Å, not 3·12 Å, as shown.)

numbered, and the small graphs in Fig. 10 show the peak position as a function of f for each peak. It is possible from these figures to deduce some general rules regarding the movement of peaks. In Fig. 11*a* the two series of reflections given by the two 'pure states' have been schematically represented by A_1, A_2,..., and B_1, B_2,.... Let us now pair off reflections of the two series, A_1 with B_2, A_3 with B_5,.... This leaves some isolated reflections, B_1 and B_4. The rules regarding shifts of peaks are found to be as follows. When the two members of a pair are close together, such as A_1, and B_2, the peak position moves almost linearly

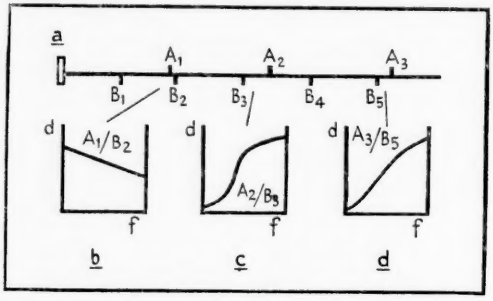

FIG. 11.

(Fig. 11*b*); more separated members (A_3 and B_5) give a slightly S-shaped curve (Fig. 11*d*); when they are far apart (A_2 and B_3) the peak position follows a markedly S-shaped curve with a steep central portion (which need not be at the position $f = 0{\cdot}5$) and almost horizontal end portions (Fig. 11*c*). At values of f corresponding to the middle portion the peak becomes very diffuse; in the end portions it is sharp. The farther apart the two members of a pair are, the greater is the slope of the central portion of the 'S', and the more diffuse is the corresponding peak. Finally, when the separation increases still farther, the two peaks may cease to form a pair, and one or both may become isolated.

In this connexion it is instructive to examine the left-hand graph in each of the series Fig. 10 *B*, *C*, *D*, *E*. These show the behaviour of the inner mica reflection in a mixture with a more hydrated component, as the spacing difference between the two components is progressively increased. With a small spacing difference (*B*), the movement of the peak is almost linear, it then becomes S-shaped (*C*); the middle part of the S becomes nearly vertical (*D*: reference to Fig. 5 will show that the peak itself becomes very diffuse in this region); finally (*E*), with a further increase in separation, the inner peak of the high-spacing component becomes isolated, and the (001) mica peak no longer shifts towards it, but to the second-order peak at 8·85 Å.

Use of curves

In the case of a random interstratification of two pure minerals, both of which are known (e.g. mica and montmorillonoid) the figures given

here may be used to determine the proportions of the constituents. For this it is only necessary to measure the positions of the peaks and compare them with those shown in the graphs. In the case of montmorillonoid mixtures it will be possible to derive additional confirmation from the effect of glycol or glycerol treatment. Inspection of Figs. 5, 6, 7, and 8 will show that where a random mixture of montmorillonoid exists, such treatment may have the effect of splitting the inner reflection into two peaks (for an actual case where this has been found to happen, see a paper by Bradley (1945)).

Where a chloritic component may be present, the effect of heating the specimen to 500° may give valuable clues. Such treatment will be expected to drive off interlamellar water molecules, and if, therefore, the characteristics of a random interstratification still persist afterwards, we may suppose that part of the interlamellar material is non-volatile, i.e. that a chloritic component is present. Comparison with Figs. 3 and 4 may then serve to give an idea of the proportion in which this component is present.

The case where a random interstratification is found to be present, but the constituents are not known, is a more complicated one. If, however, the mixture which exists is one of those covered by the present graphs, it should be possible to identify it. It has also been pointed out by Méring (1949) that the problem of finding out what 'pure states' are present, and in what proportions, can in theory be solved by forming the Fourier transform of the scattering function. This method suffers from several difficulties:

1. The scattering function cannot usually be experimentally determined over a sufficiently large range of equivalent spacings.
2. The scattering factor of the layers drops to zero at certain points, and in the neighbourhood of these points the scattering function is not even in theory determinable.
3. Even in points where the scattering can be measured, the background scattering cannot readily be allowed for.

These difficulties may not be insuperable, but at present the problem of determining the constituents and proportions of an unknown mixture will be best approached from the other end by calculating the scattering to be expected from various mixtures, assumed *a priori*.

It has been pointed out that, in general, broad bands are not given by two-component interstratifications of the type considered here. Such bands are, however, commonly given by soil clay minerals, and where they are present we may suspect that some more complicated type of mixture is present, e.g. one of type 3. Some such cases have been considered in the previous paper (MacEwan, 1949).

Acknowledgements

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MATHEMATICAL APPENDIX

An account is given here of the derivation of formula (1).

The first factor F_l^2 is calculated from the formula

$$F_l = \sum_r n_r F_a^r \cos 2\pi \frac{z_r}{d'}, \tag{2}$$

where n = number of atoms or ions of type r;

F_a^r = atomic scattering factor of atoms or ions of type r (this is, of course, a function of d');

z_r = co-ordinate, in a direction perpendicular to the layers, of the atoms or ions of type r;

d' has already been defined (formula (1)).

Here the one-dimensional projection of the structure is assumed to have a centre of symmetry, and z_r is measured from this centre of symmetry.

In applying this formula, positions were assumed for the atoms or ions corresponding to the published structures of muscovite, biotite, and kaolinite.

The second factor in formula (1) has already been dealt with. We now give a full derivation of the third factor, that which takes account of the random nature of the structure.

This is given by the final formula in section 2 of Hendricks and Teller's paper as follows:

$$\frac{1-C^2}{1-2C\cos\bar{\phi}+C^2}, \tag{3}$$

where

$$C = \sum_1^r{}_s f^s \cos(\phi^s - \bar{\phi}),$$

there being supposed to exist r components, with frequencies f^s, where, of course,

$$\sum_1^r{}_s f^s = 1.$$

The corresponding phase changes are ϕ^s.

Our treatment is based on formula (3), above, for the case of only two components with frequencies f and $1-f$. In this case, therefore,

$$C = f\cos(\phi^1-\bar{\phi})+(1-f)\cos(\phi^2-\bar{\phi}), \tag{4}$$

and from Hendricks and Teller's equation (7):

$$f\sin(\phi^1-\bar{\phi})+(1-f)\sin(\phi^2-\bar{\phi}) = 0. \tag{5}$$

Now the phase difference due to a layer of spacing d_1 is

$$2\pi\frac{2d_1\sin\theta}{\lambda}, \quad \text{and} \quad \lambda = 2d'\sin\theta.$$

$\therefore$ Phase difference for d_1 is

$$\phi^1 = 2\pi\frac{2d_1\sin\theta}{2d'\sin\theta} = 2\pi\frac{d_1}{d'}. \tag{6}$$

Similarly

$$\phi^2 = 2\pi\frac{d_2}{d'}.$$

Now $C^2 = f^2\cos^2(\phi^1-\bar{\phi})+(1-f)^2\cos^2(\phi^2-\bar{\phi})+2f(1-f)\cos(\phi^1-\bar{\phi})\cos(\phi^2-\bar{\phi}).$

Let

$$\phi^1-\bar{\phi} = A, \qquad \phi^2-\bar{\phi} = B.$$

Then

$$\begin{aligned} C^2 &= f^2(1-\sin^2A)+(1-f)^2(1-\sin^2B)+2f(1-f)\cos A\cos B \\ &= f^2+(1-f)^2-f^2\sin^2A-(1-f)^2\sin^2B+2f(1-f)\cos A\cos B. \end{aligned} \tag{7}$$

Now from (5)

$$f^2\sin^2A+(1-f)^2\sin^2B = -2f(1-f)\sin A\sin B.$$

$$\therefore \quad C^2 = f^2+(1-2f+f^2)+2f(1-f)(\sin A\sin B+\cos A\cos B)$$
$$= 1-2f(1-f)+2f(1-f)\cos(B-A)$$
$$= 1-2f(1-f)\left(1-\cos 2\pi\frac{d_2-d_1}{d'}\right) \quad \text{(substituting from (6))}$$
$$= 1-4f(1-f)\sin^2\pi\frac{d_2-d_1}{d'}. \qquad (8)$$

Now $$C\cos\bar{\phi} = [f\cos(\phi^1-\bar{\phi})+(1-f)\cos(\phi^2-\bar{\phi})]\cos\bar{\phi}.$$

Making use of the identity

$$\cos x\cos y = \cos(x+y)+\sin x\sin y,$$

we can put this into the form

$$f\cos\phi^1+(1-f)\cos\phi^2+[f\sin(\phi^1-\bar{\phi})+(1-f)\sin(\phi^2-\bar{\phi})]\sin\bar{\phi},$$

and the portion in square brackets is zero, by (5). Thus we get

$$C\cos\bar{\phi} = f\cos 2\pi\frac{d_1}{d'}+(1-f)\cos 2\pi\frac{d_2}{d'}.$$

Substituting for $1-C^2$ and $1+C^2$ from (8), we get finally after dividing numerator and denominator by 2:

$$\frac{1-C^2}{1-2C\cos\bar{\phi}+C^2} = \frac{2f(1-f)\sin^2\pi\dfrac{d_2-d_1}{d'}}{1-2f(1-f)\sin^2\pi\dfrac{d_2-d_1}{d'}-f\cos 2\pi\dfrac{d_1}{d'}-(1-f)\cos 2\pi\dfrac{d_2}{d'}}.$$

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